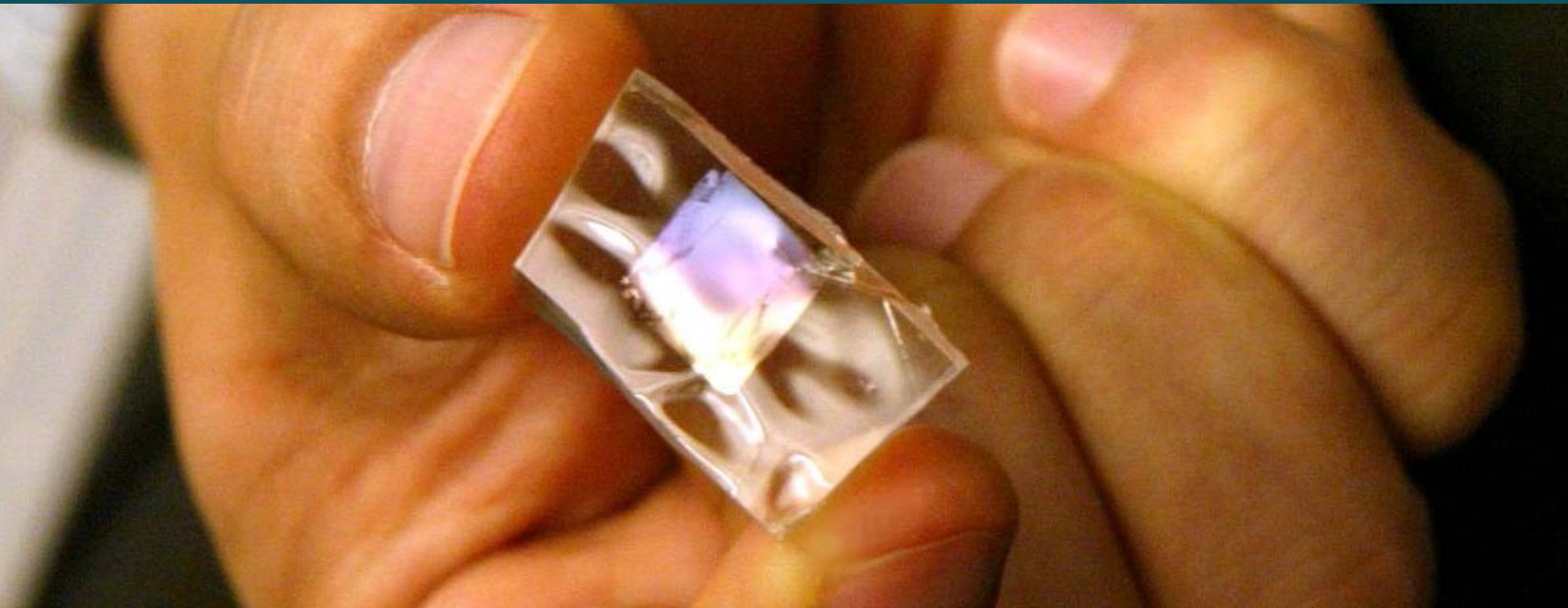


| REPORT DOCUMENTATION PAGE   |             |                                   |                               |                                      | Form Approved<br>OMB No. 0704-0188                        |  |
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| 1. REPORT DATE (DD-MM-YYYY)<br>08/06/2012   |             | 2. REPORT TYPE<br>Final Technical |                               |                                      | 3. DATES COVERED (From - To)<br>05/05/2010 -05/04/2012    |  |
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|   |             |                                   |                               | 5b. GRANT NUMBER<br>N66001-10-1-2012 |   |  |
|   |             |                                   |                               | 5c. PROGRAM ELEMENT NUMBER           |   |  |
| 6. AUTHOR(S)<br>Michael McAlpine  |             |                                   |                               | 5d. PROJECT NUMBER                   |   |  |
|   |             |                                   |                               | 5e. TASK NUMBER                      |   |  |
|   |             |                                   |                               | 5f. WORK UNIT NUMBER                 |   |  |
| 7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)<br>The Trustees of Princeton University<br>4 New South Building<br>P O Box 36<br>Princeton, NJ 08544   |             |                                   |                               |                                      | 8. PERFORMING ORGANIZATION<br>REPORT NUMBER<br><br>N/A    |  |
| 9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)<br>Space and Naval Warfare Systems Command  |             |                                   |                               |                                      | 10. SPONSOR/MONITOR'S ACRONYM(S)<br><br>SPAWAR            |  |
|   |             |                                   |                               |                                      | 11. SPONSOR/MONITOR'S REPORT<br>NUMBER(S)                 |  |
| 12. DISTRIBUTION/AVAILABILITY STATEMENT<br>Available to the Public  |             |                                   |                               |                                      |   |  |
| 13. SUPPLEMENTARY NOTES   |             |                                   |                               |                                      |   |  |
| 14. ABSTRACT<br>The objective of this proposal is the hierarchical assembly of piezoelectric and semiconducting ribbons onto a common polymeric platform for thin, flexible energy harvesting. In particular, we aim to reach a target output of 5 mW at 100 Hz. The development of a method for integrating highly efficient energy conversion materials onto stretchable, biocompatible rubbers could yield breakthroughs in implantable or wearable energy harvesting systems. Being electromechanically coupled, piezoelectric crystals represent a particularly interesting subset of smart materials which function as sensors/actuators, bioMEMS devices, and energy converters. Yet, the crystallization of these materials generally requires high temperatures for maximally efficient performance, rendering them incompatible with with temperature-sensitive plastics and rubbers. Here, we propose overcoming these limitations by presenting a scalable and parallel process for transferring crystalline piezoelectric ribbons of lead zirconate titanate (PZT) from host substrates onto flexible plastics over macroscopic areas. The ribbons are fabricated from single crystal, stoichiometric films of PZT, allowing for exceptional control over the composition and, consequently, the performance characteristics of these materials. |             |                                   |                               |                                      |   |  |
| 15. SUBJECT TERMS<br>Nanotechnology, Electromechanical energy harvesting, Biocompatible piezoelectrics, Nanomaterials   |             |                                   |                               |                                      |   |  |
| 16. SECURITY CLASSIFICATION OF:   |             |                                   | 17. LIMITATION OF<br>ABSTRACT | 18. NUMBER<br>OF<br>PAGES            | 19a. NAME OF RESPONSIBLE PERSON                           |  |
| a. REPORT   | b. ABSTRACT | c. THIS PAGE                      |                               |                                      | Michael McAlpine  |  |
| U   | U           | U                                 | UU                            | 45                                   | 19b. TELEPHONE NUMBER (Include area code)<br>609-542-0275 |  |

Reset

# Biointerfaced Nanopiezoelectrics



**Michael McAlpine**  
**Princeton University**

# Milestones (5/5/10–5/5/12)

| <i>Tasks</i>   | <i>Accomplishments</i>  |
|--|---|
| <p><b>1 – PZT Ribbon Fabrication</b></p> <p>(a) Optimize film growth<br/>(b) Fabrication of ribbons</p>  | <p><b>1 – PZT Ribbon Fabrication</b></p> <p>✓ Single-crystal, stoichiometric films have been grown and nanoribbons defined over 2" diameter areas</p>   |
| <p><b>2 – PZT Ribbon Transfer to Plastic</b></p> <p>(a) Optimize transfer to flexible substrates<br/>(b) Scale transfer process to 2" areas</p>          | <p><b>2 – PZT Ribbon Transfer to Plastic</b></p> <p>✓ We have been able to achieve transfer onto a variety of substrates, including elastomers, plastics, and silk, over 2" diameter areas</p>    |
| <p><b>3 – Charge Constant Metrics</b></p> <p>(a) Maximize <math>d_{33}</math> on MgO by PFM<br/>(b) Maximize <math>d_{33}</math> on plastic by PFM</p>   | <p><b>3 – Charge Constant Metrics</b></p> <p>✓ We have achieved the highest piezoelectric charge constant (<math>d_{33} = 150</math> pm/V) ever on a flexible platform</p>                        |
| <p><b>4 – PZT Energy Harvesting Device</b></p> <p>(a) Interdigitated electrode fabrication<br/>(b) Power output test</p>                                 | <p><b>4 – PZT Energy Harvesting Device</b></p> <p>✓ Achieved voltage outputs of 1.5 V (peak-to-peak) and power outputs of 10 mW/cm<sup>3</sup> in both stretching and flexing operation modes</p> |
| <p><b>5 – Heterogeneous Interfacing With Body</b></p> <p>(a) Integration of piezoelectric nanomaterials directly with the body for energy harvesting</p> | <p><b>5 – Heterogeneous Interfacing with Body</b></p> <p>✓ Demonstrated interfacing with cells, and direct biointerfacing with cow lungs for implantable on-body energy harvesting</p>            |

# Return on Investment – 1

- Total # of people employed: 1 Faculty (Prof. Michael C. McAlpine), 1 graduate student (Thanh Nguyen, graduating 6/2013), 2 postdocs (Dr. Yi Qi, now at GLOBALFOUNDRIES; Dr. Jihoon Kim, now at AZ Electronic Materials)
- # of new hires as a result of this funding: 1 (Dr. Jihoon Kim)
- # of newly trained scientists in this area: 3 (Nguyen, Kim, Qi)
- # of PhD theses initiated based on this work: 0 (I have only been as assistant professor for 4 years, not long enough to graduate someone yet)
- Discoveries utilized on other efforts / Follow-on funding: The results that we have achieved have led directly to a number of new projects and funding:
  - Army Research Office, “Buckled Piezoelectric Nanoribbons: Morphology, Nanomechanics, and Flexoelectricity,” \$120k/yr for 3 yrs (\$360k total)
  - Lockheed Martin, “Investigation of Wireless Energy Harvesting,” \$50k total
  - Essig-Enright and Insley Blair Pyne Funds, “Studying Neuron Biomechanics via Interfacing with Piezoelectric Nanowires,” \$52.5k/yr for 2 yrs (\$105k total)
- Patents Filed: 2
  - M. C. McAlpine, Y. Qi. Buckled and Wavy Piezoelectric Ribbons for Stretchable Energy Harvesting Devices. U.S. Patent Pending 61/422,808.
  - M. C. McAlpine, Y. Qi. Flexible Piezoelectric Structures and Method of Making Same. U.S. Patent Pending 12/727,798.



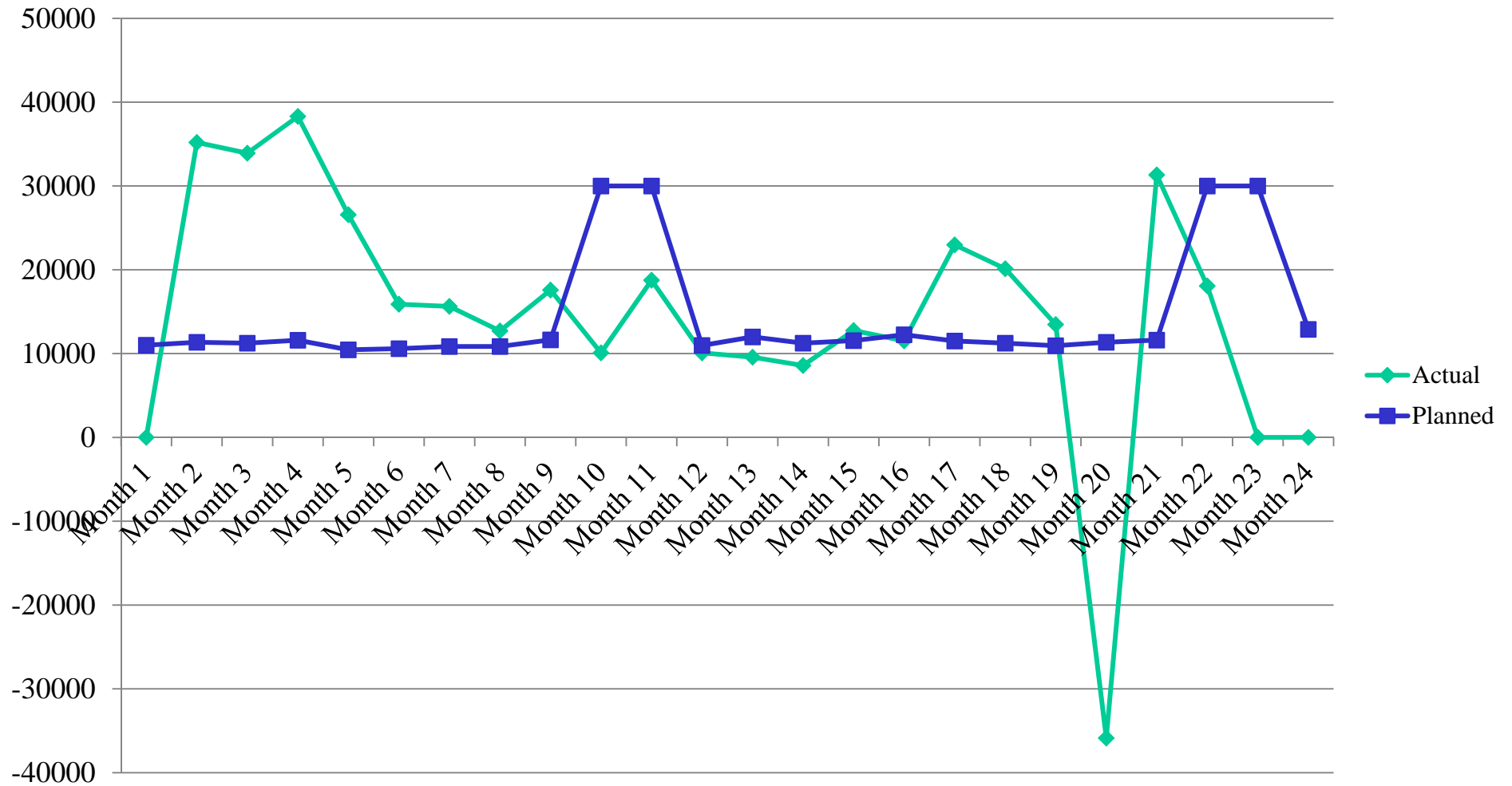
# Return on Investment – 2

- Papers and Books Published: 6 total:
  - T. D. Nguyen, N. Deshmukh, J. M. Nagarah, T. Kramer, P. K. Purohit, M. J. Berry, M. C. McAlpine. "Piezoelectric Nanoribbons for Interfaced Cellular Nanomechanics." *Nature Nanotechnology* (2012).
  - Y. Qi, T. D. Nguyen, J. Kim, M. C. McAlpine. "Stretchable Piezoelectric Nanoribbons for Biocompatible Energy Harvesting." Invited Book Chapter, in Stretchable Electronics, ed. Takao Someya (2013).
  - Y. Qi, J. Kim, T. D. Nguyen, B. Lisko, P. K. Purohit, M. C. McAlpine. "Enhanced Piezoelectricity and Stretchability in Energy Harvesting Devices Fabricated from Buckled PZT Ribbons." *Nano Lett.* **11**, 1331-1336 (2011). [Featured in *Nature*: M. H. Lee, A. Javey. "Power Surfing on Waves." *Nature* **472**, 304-305 (2011).]
  - T. D. Nguyen, J. M. Nagarah, Y. Qi, S. S. Nonnenmann, A. V. Morozov, S. Li, C. B. Arnold, M. C. McAlpine. "Wafer-Scale Nanopatterning and Translation into High Performance Piezoelectric Nanowires." *Nano Lett.* **10**, 4595-4599 (2010).
  - Y. Qi, M. C. McAlpine. "Nanotechnology-Enabled Flexible and Biocompatible Energy Harvesting." *Energy Environ. Sci.* **3**, 1275-1285 (2010).
  - Y. Qi, N. T. Jafferis, K. Lyons, Jr., C. M. Lee, H. Ahmad, M. C. McAlpine. "Piezoelectric Ribbons Printed onto Rubber for Flexible Energy Conversion." *Nano Lett.* **10**, 524-528 (2010).

# Return on Investment – 3

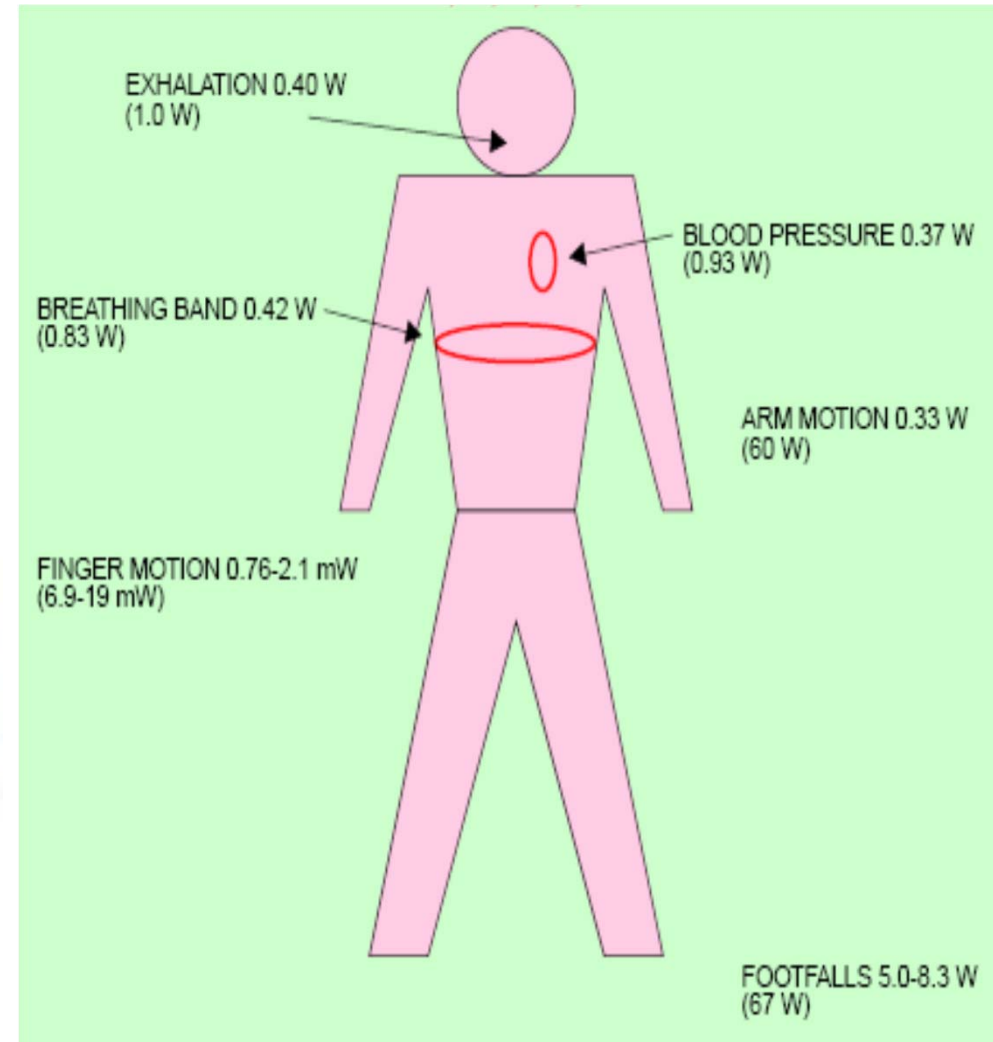
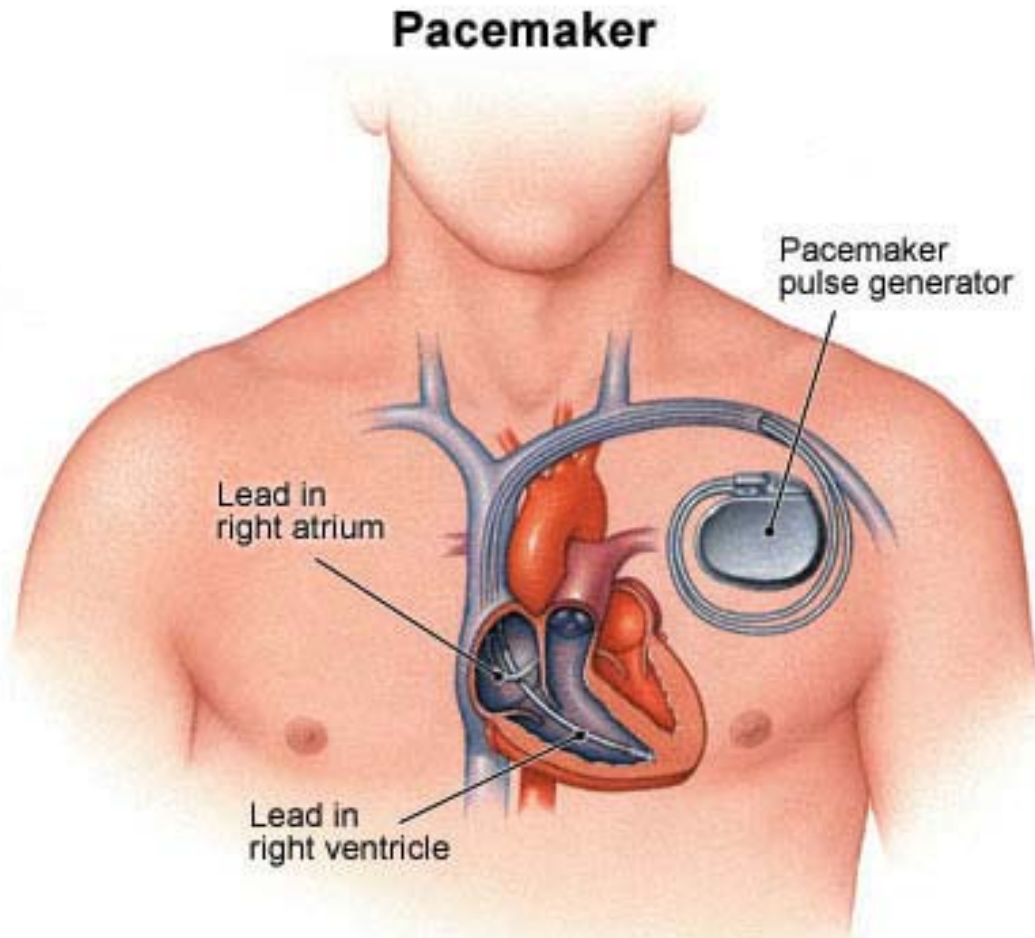
- Invited Presentations Related to This Work:
- 19. "Biointerfaced Nanodevices," New York University, 10/31/12 (New York, NY).
- 18. "Biointerfaced Nanodevices," University of California - Berkeley, 10/2/12 (Berkeley, CA).
- 17. "Biointerfaced Nanodevices," Microsoft Research, 6/11/12 (Redmond, WA).
- 16. "Nanotechnology-Enabled Advances in Piezoelectric Energy Harvesting," ONR International Workshop on Acoustic Transduction Materials and Devices, 5/10/12 (State College, PA).
- 15. "Nanotechnology-Enabled Advances in Biomedical and Energy Research," University of Pennsylvania, 4/24/12 (Philadelphia, PA).
- 14. "Nanotechnology-Enabled Advances in Biomedical and Energy Research," University of Texas at Austin, 3/28/12 (Austin, TX).
- 13. "Nanotechnology-Enabled Advances in Biomedical and Energy Research," Georgia Institute of Technology, 3/19/12 (Atlanta, GA).
- 12. "Nanotechnology-Enabled Advances in Biomedical and Energy Research," University of Illinois at Urbana-Champaign, 2/16/12 (Urbana-Champaign, IL).
- 11. "Nanotechnology-Enabled Device Interfacing with the Human Body," Drexel University, 11/10/11 (Cherry Hill, NJ).
- 10. "Nanotechnology-Enabled Device Interfacing with the Human Body," Lockheed Martin Advanced Technology Laboratories, 10/28/11 (Cherry Hill, NJ).
- 9. "Nanotechnology-Enabled Device Interfacing with the Human Body," DuPont Central Research and Development, 6/25/11 (Wilmington, DE).
- 8. "Nanotechnology-Enabled Device Interfacing with the Human Body," Keynote Speech at Freescale Technology Forum, 6/22/11 (San Antonio, TX).
- 7. "Nanotechnology-Enabled Interfacing of Devices with the Human Body," Google Tech Talk, 6/6/11 (Mountain View, CA).
- 6. "Nanotechnology-Enabled Flexible Energy Harvesting," SPIE Defense, Security, and Sensing Conference, 4/28/11 (Orlando, FL).
- 5. "Nanotechnology-Enabled Flexible Energy Harvesting," Materials Research Society (MRS) Fall Conference, 12/1/10 (Boston, MA).
- 4. "Nanotechnology-Enabled Flexible Energy Harvesting," IDTechEx Energy Harvesting & Storage USA, 11/17/10 (Boston, MA).
- 3. "Nanotechnology-Enabled Flexible Energy Harvesting," Technology Review EmTech@MIT 2010 Conference, 9/23/10 (Cambridge, MA).
- 2. "Nanotechnology-Enabled Flexible Energy Harvesting," Workshop on Nanomaterials for Alternative Energy Applications, University of British Columbia, 6/21/10 (Vancouver, BC, Canada).
- 1. "Nanotechnology-Enabled Flexible Energy Harvesting," Princeton Technology Center, Schlumberger, 6/3/10 (Princeton, NJ).

# Spend Chart



Financials: 1) Percent of funds expended: **100%**, 2) Total of funds expended: **\$347,193**, 3) Total of funds remaining: **\$0**

# Human Power



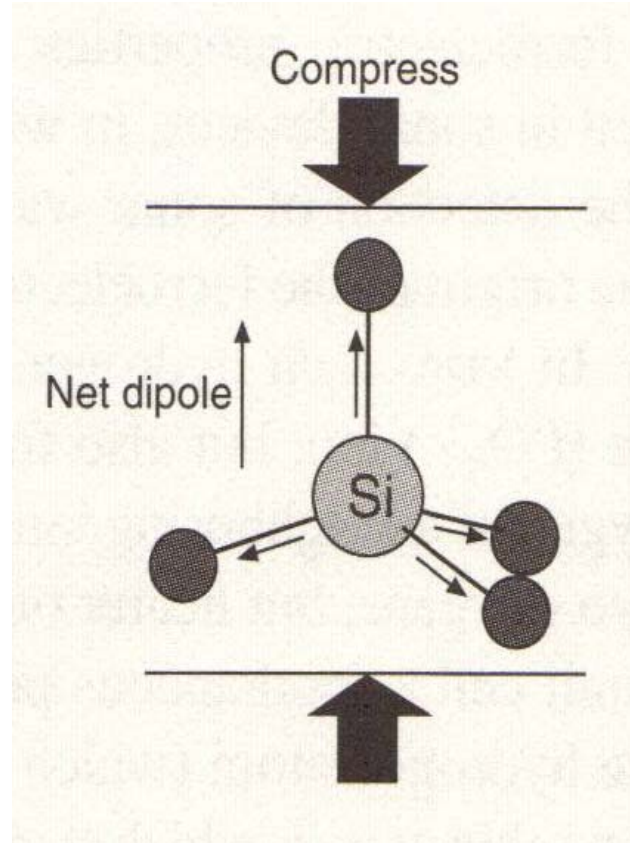
T. Starner, *IBM Syst J* 35, 618–629 (1996)

# Piezoelectricity

Mechanical Energy



Sensor



Actuator



Electrical Energy



# Energy

$$E \propto d_{33}^2 \sigma^2 V$$

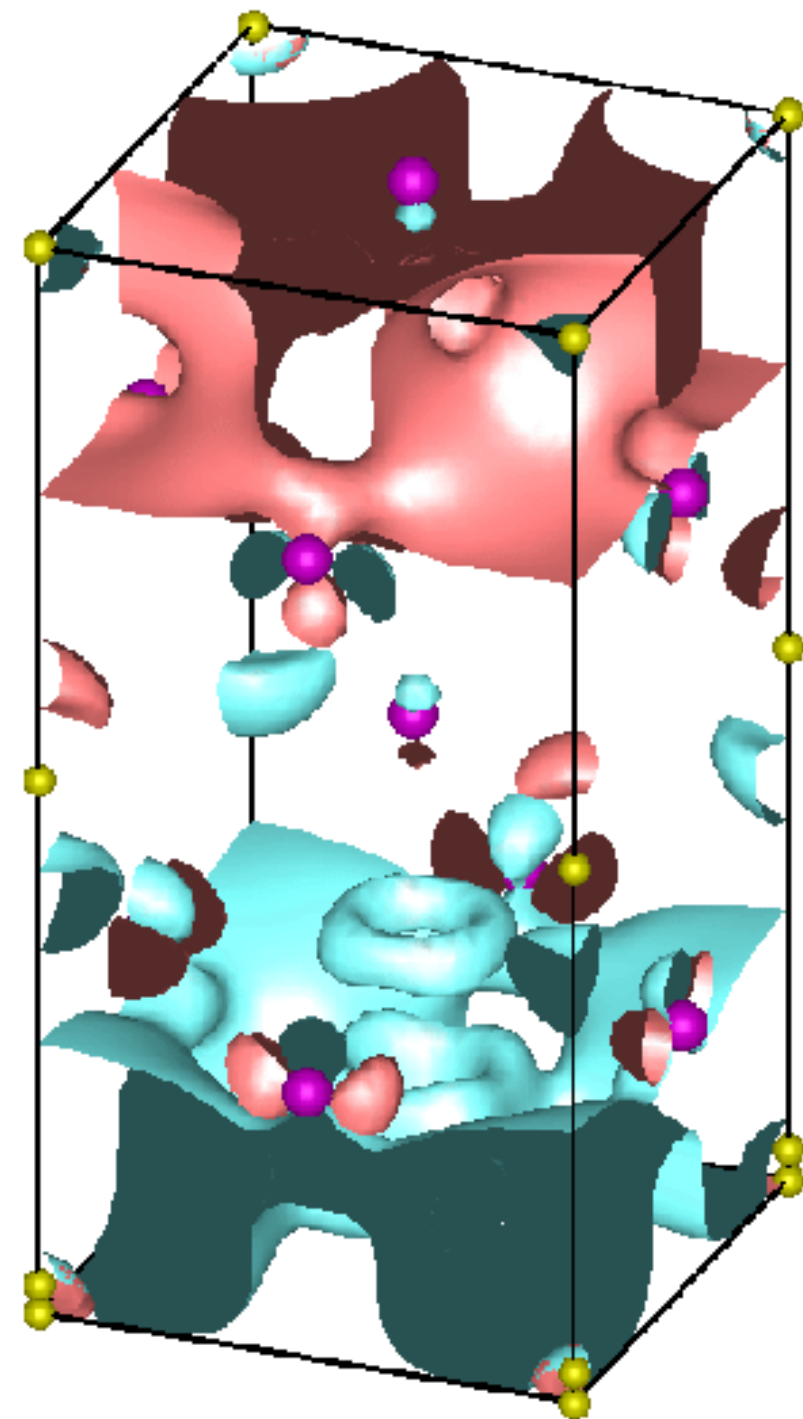
| $d_{33}$<br>(pm/V) | PZT | PVDF | Quartz | Bone |
|--------------------|-----|------|--------|------|
|                    | 250 | 25   | 2.5    | .25  |

$$k_{33} \propto d_{33}$$

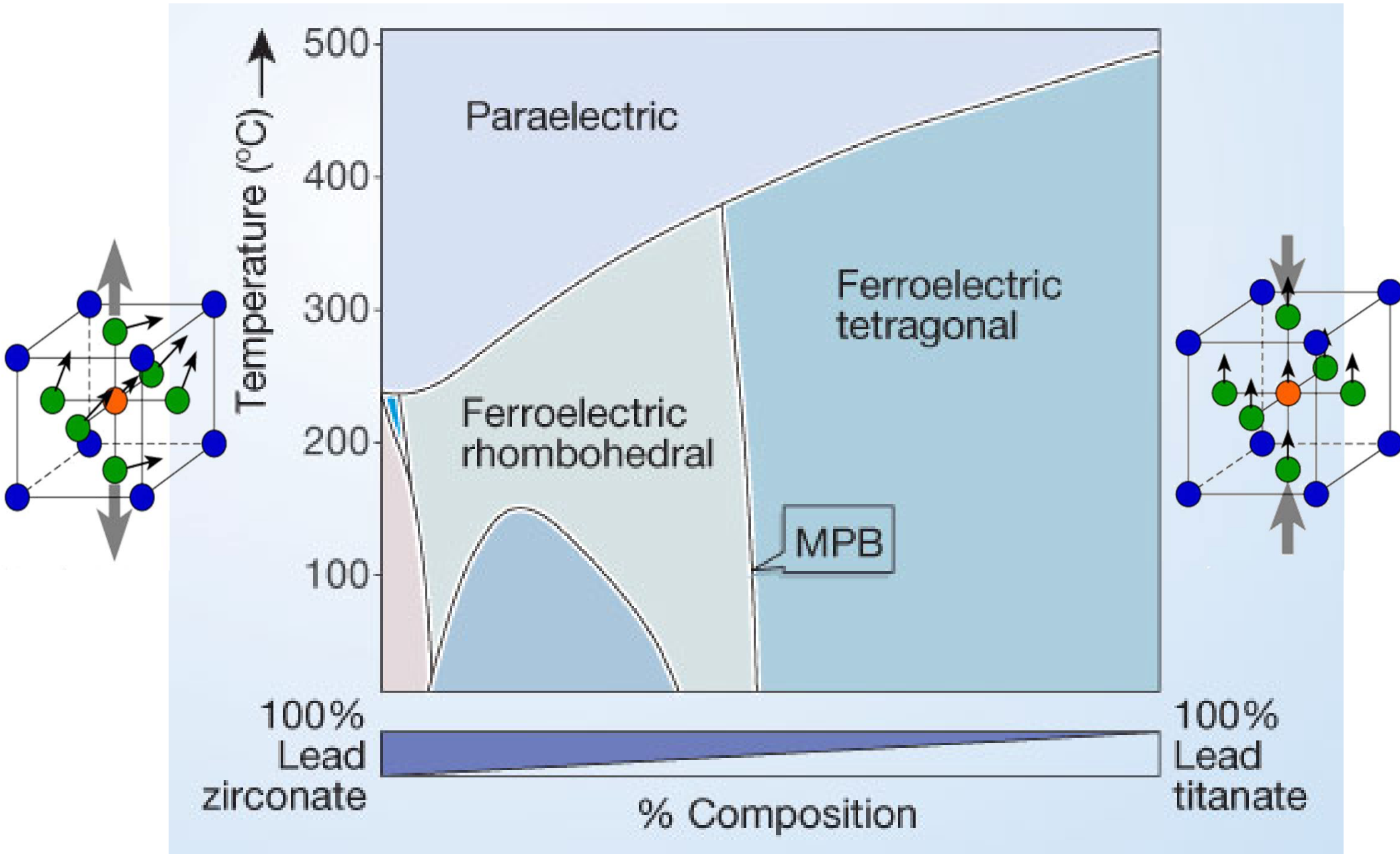
PZT > 80% Conversion Efficiency

S. R. Platt, *et al*, *IEEE Trans Mech* 10, 240-252 (2005)

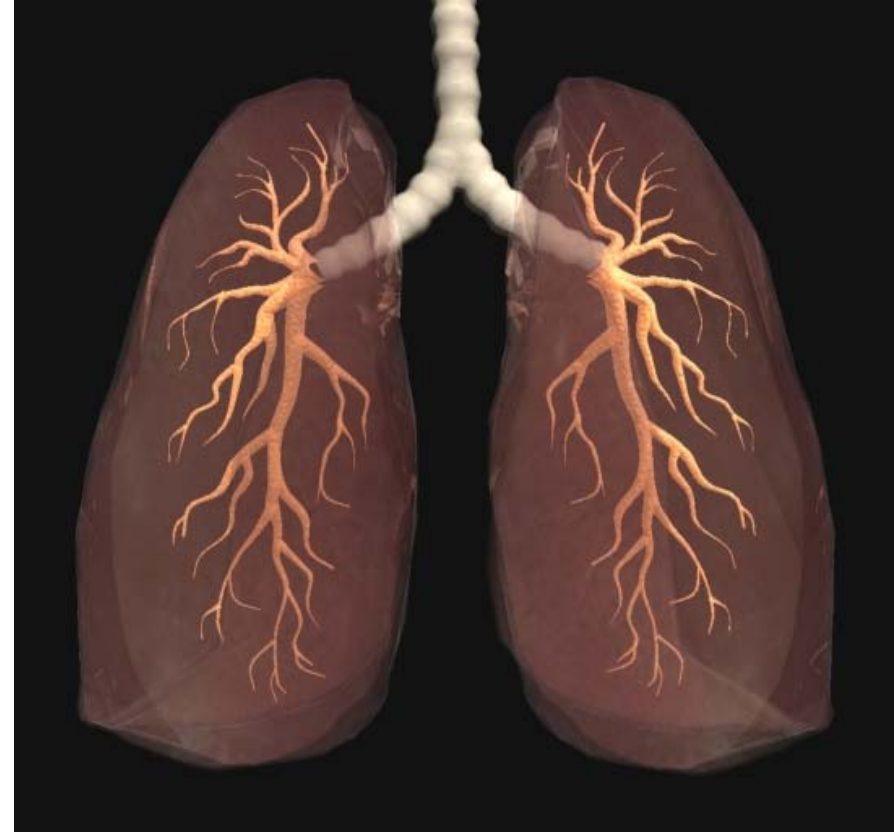
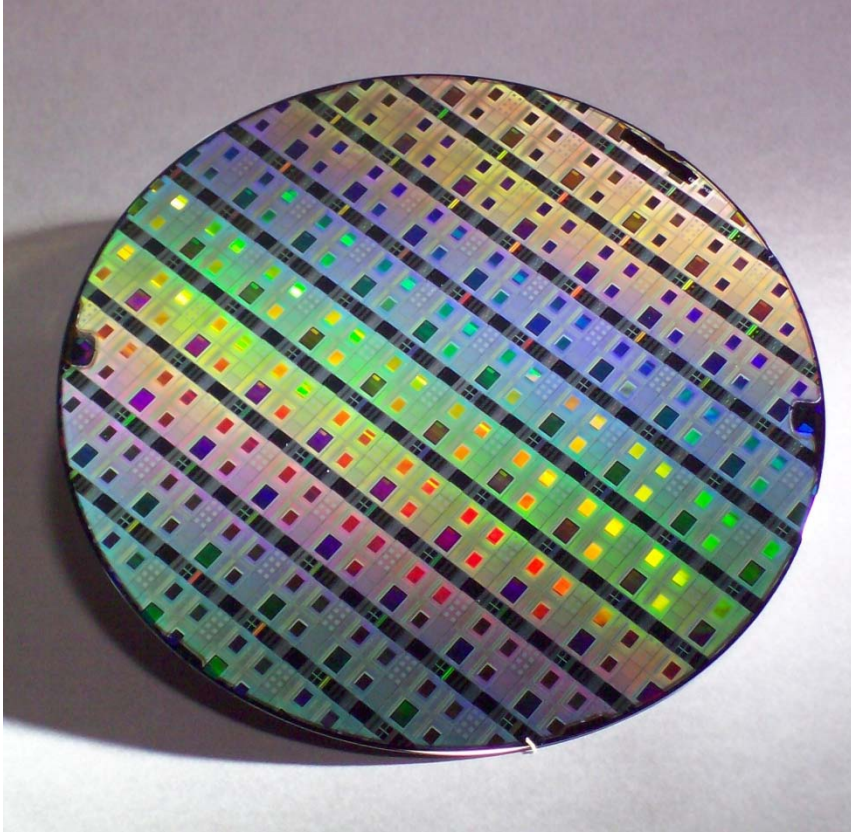
# PZT



# Phase Diagram

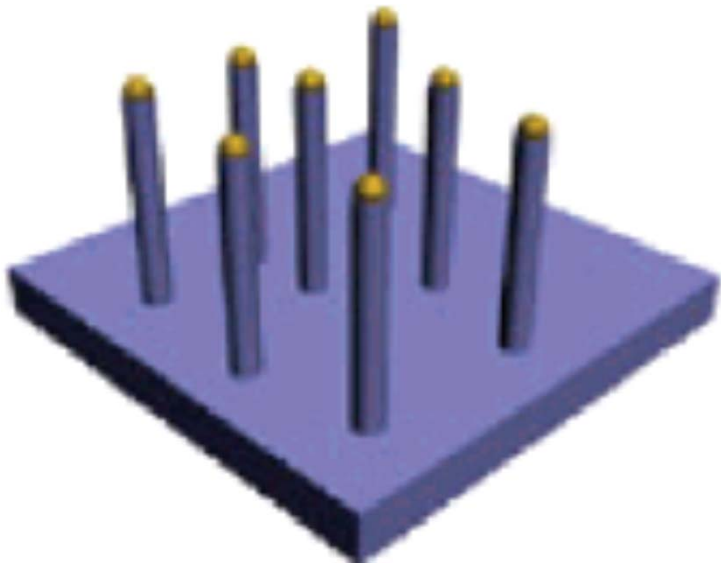


# Dichotomy



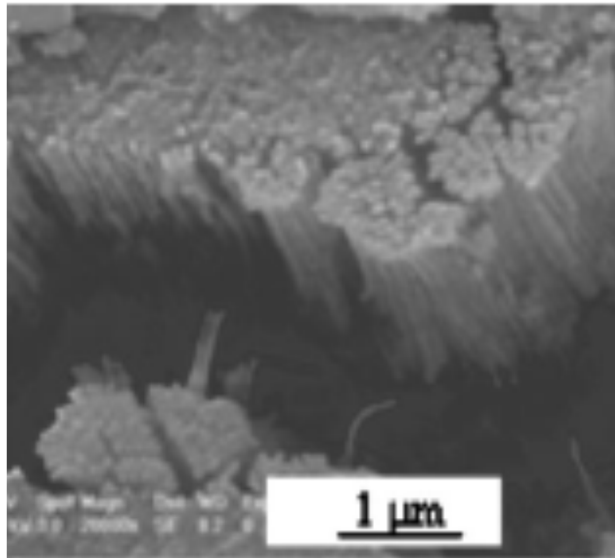
# PZT Nanowires

**VLS Growth –  
Lack of Catalysts**



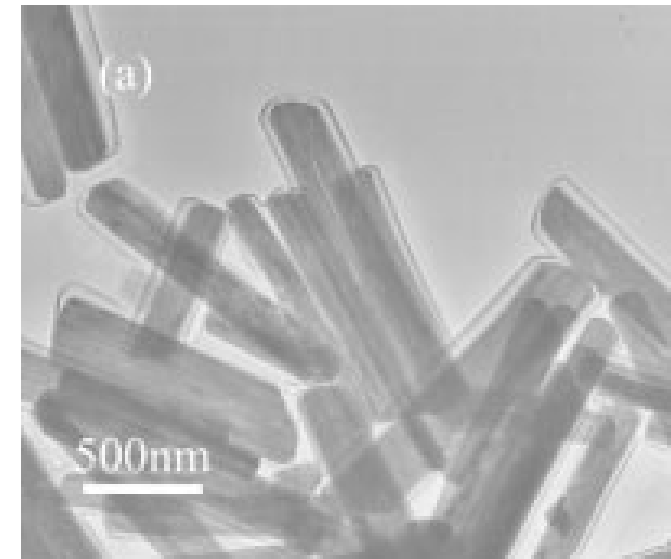
**C. Zhou, et al, *Nano Lett*  
4, 1241-1246 (2004)**

**Confined Templates –  
Polycrystallinity**



**M. Alexe, et al, *Appl Phys  
Lett* 83, 440 (2003)**

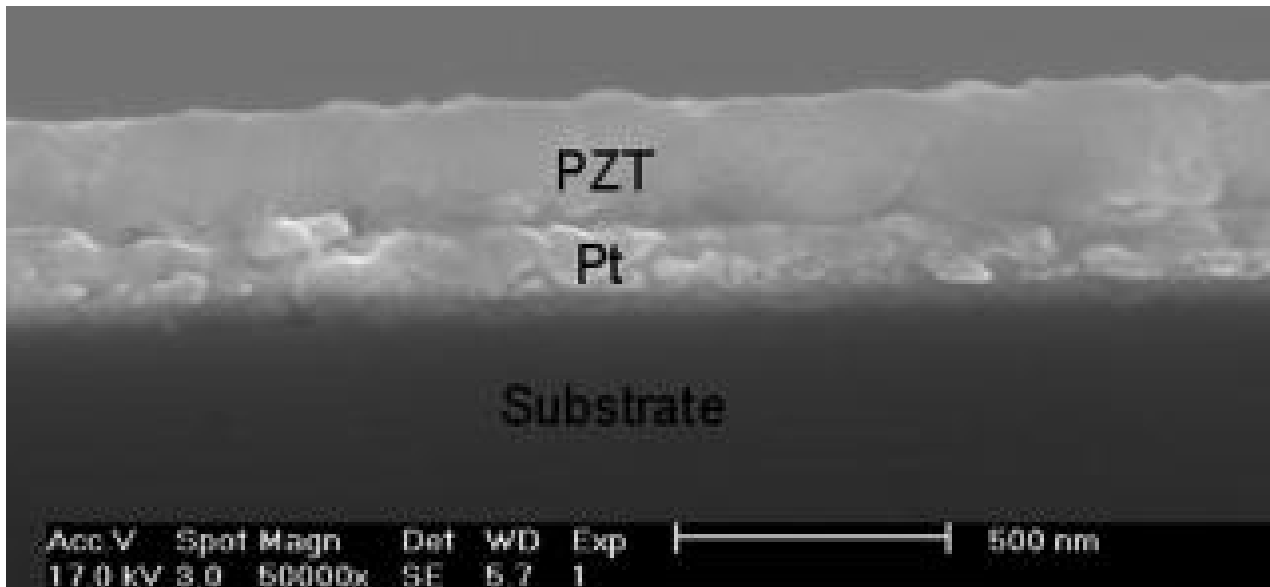
**Hydrothermal –  
Stoichiometry**



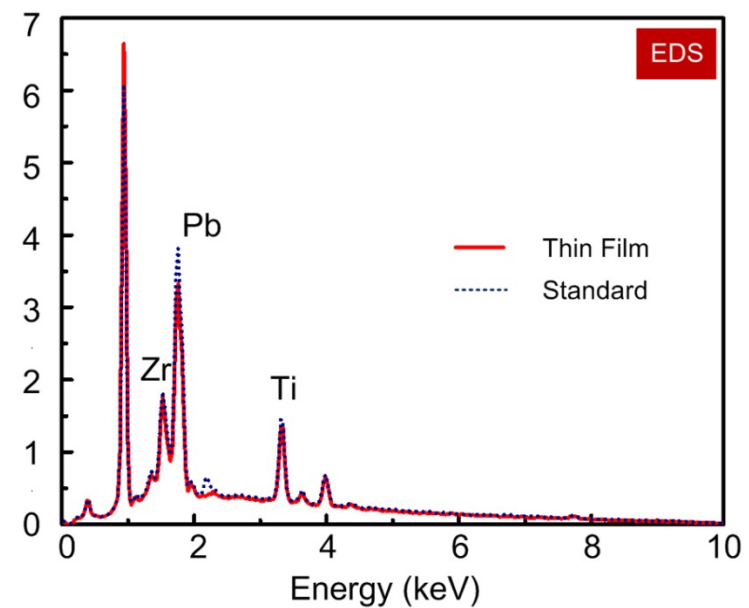
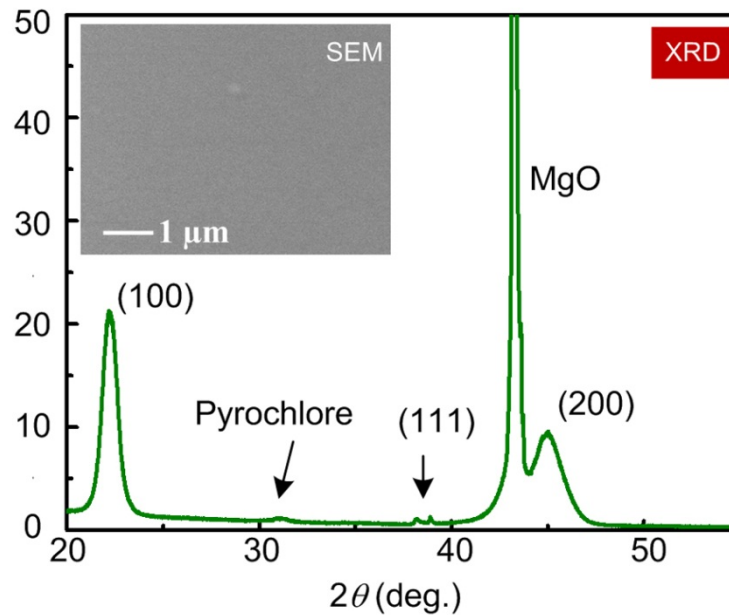
**G. Han, et al, *Adv Mater*  
17, 907-910 (2005)**



# Thin Film

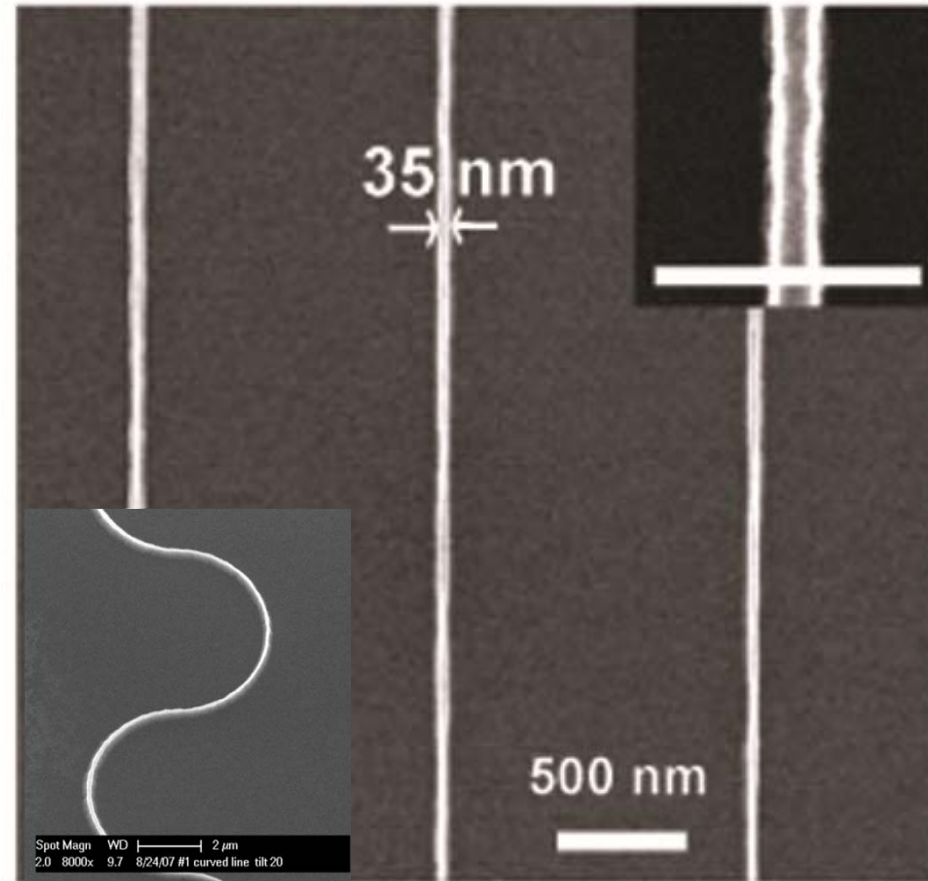
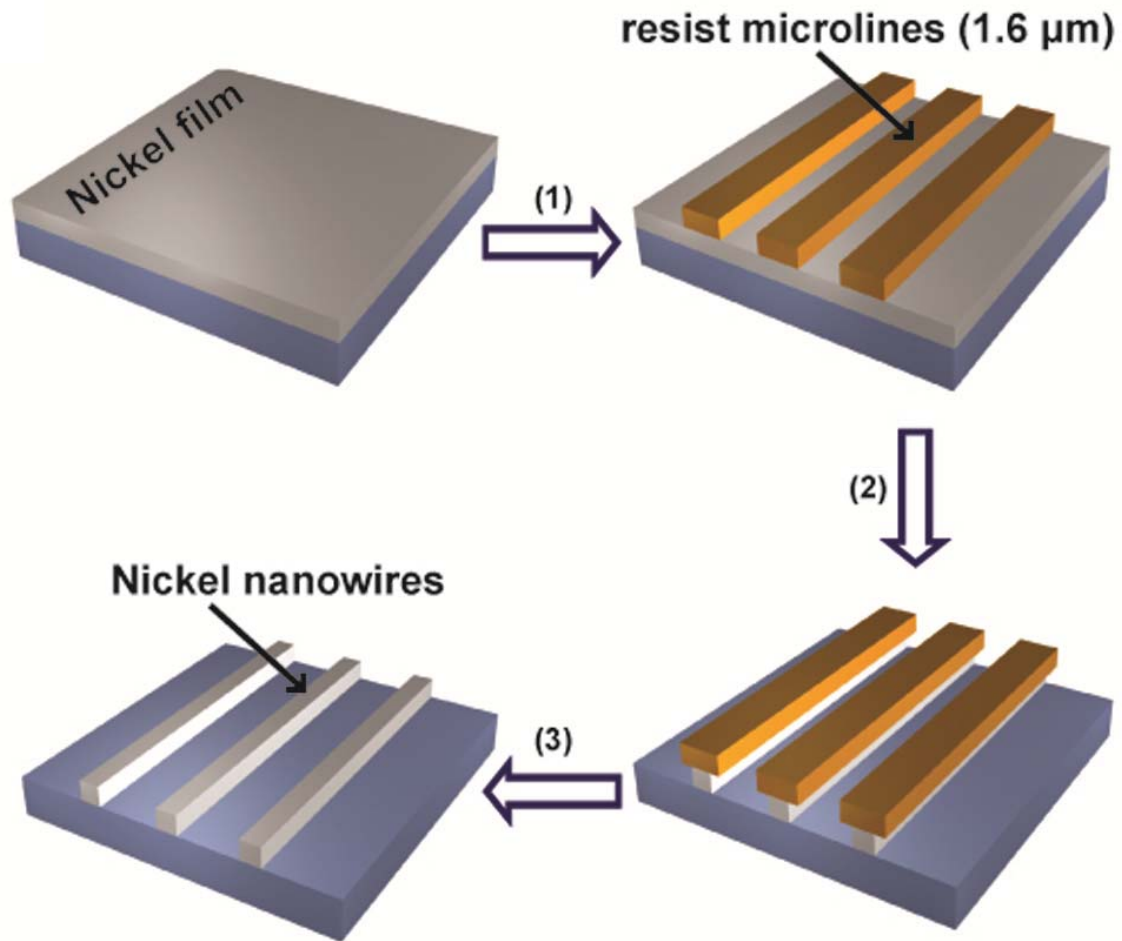


|                    |      |
|--------------------|------|
| MgO                | 4.21 |
| PZT                | 4.05 |
| SrTiO <sub>3</sub> | 3.91 |

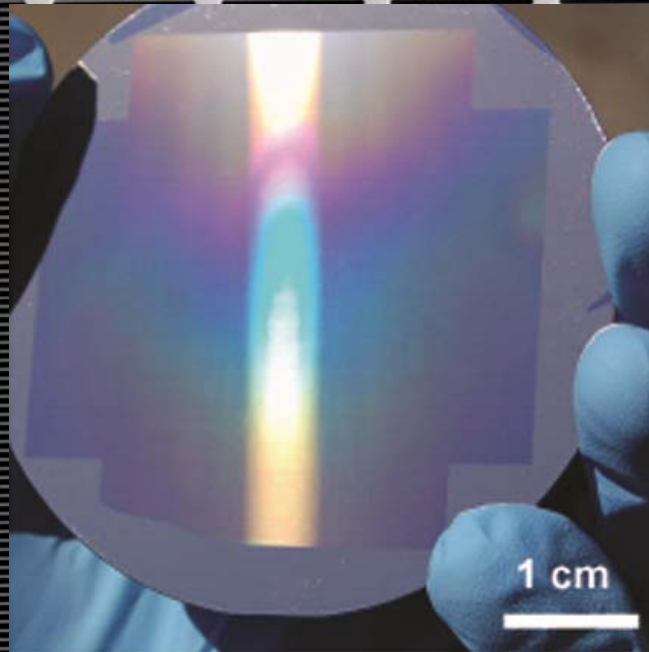


**Post-anneal at 700 °C**

# PENCiL



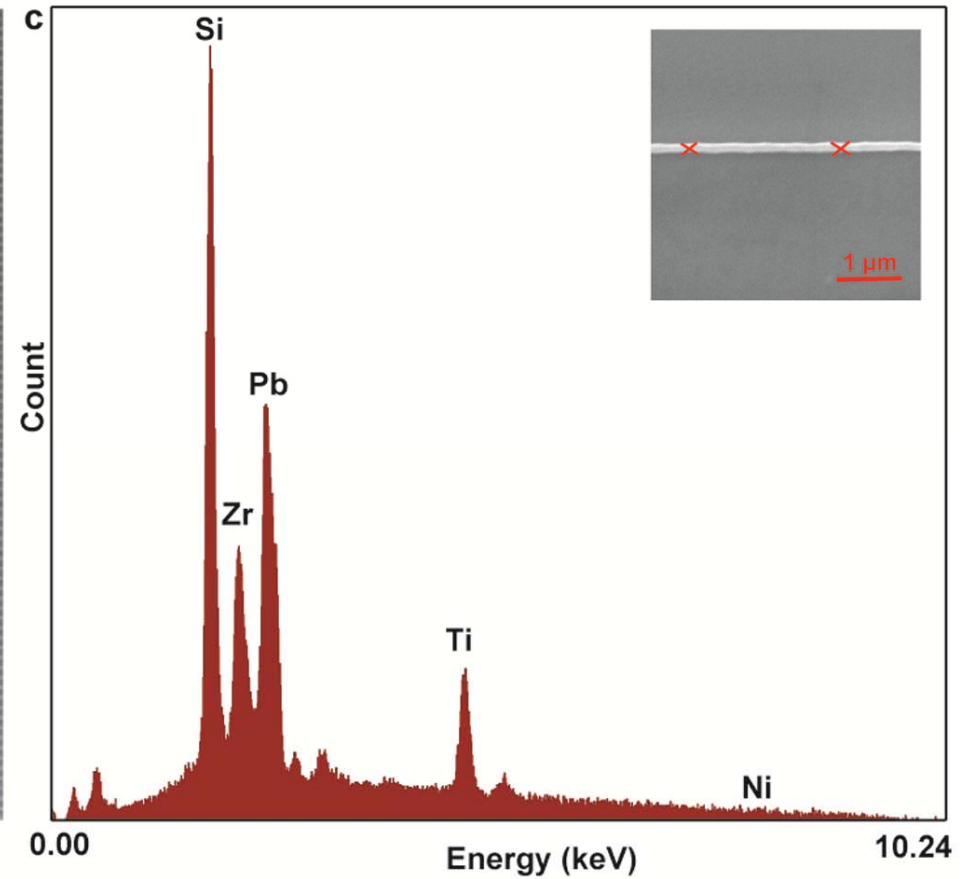
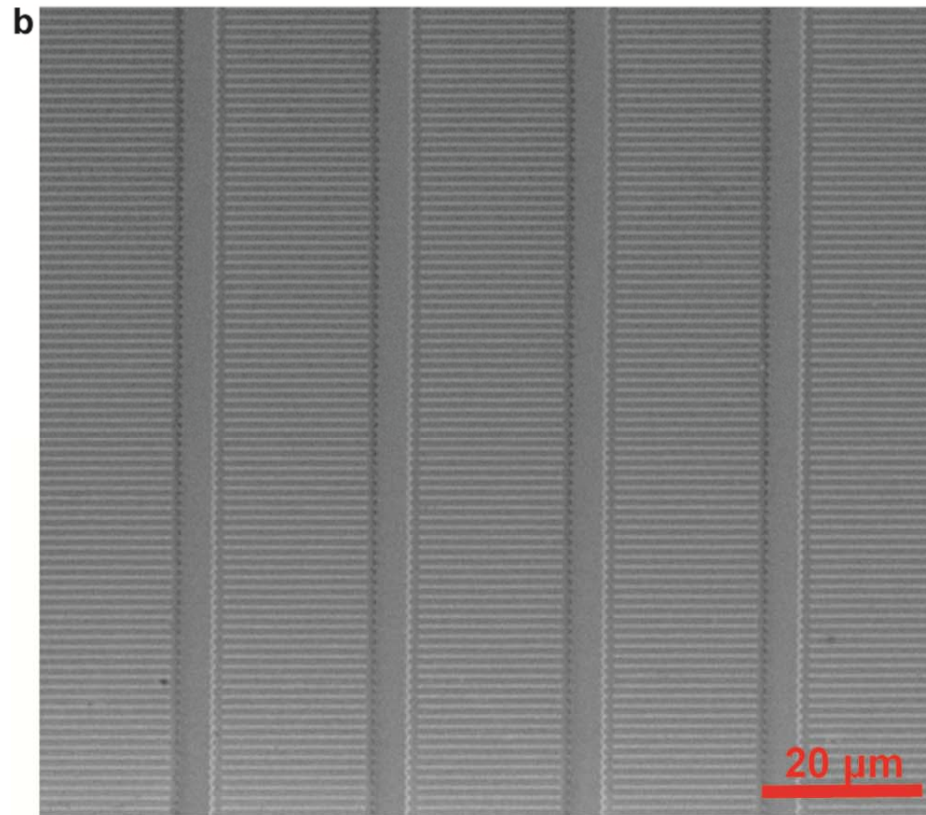
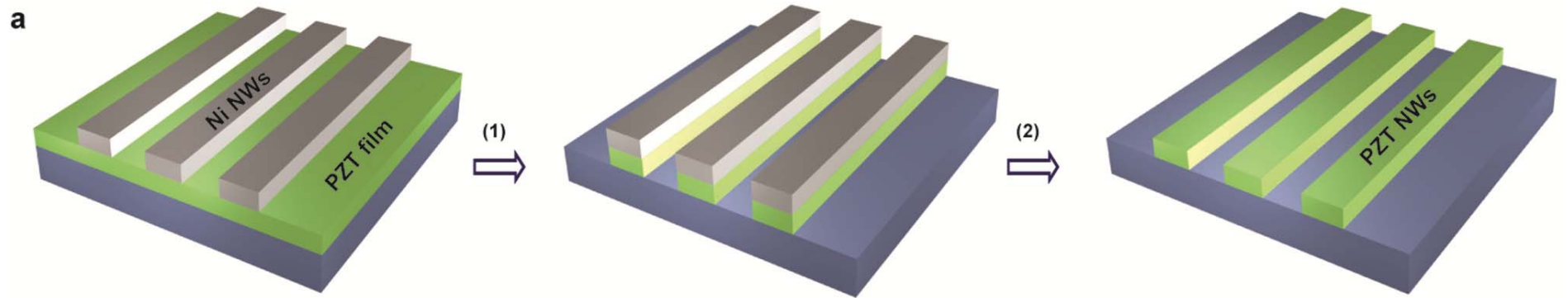
# Wafer



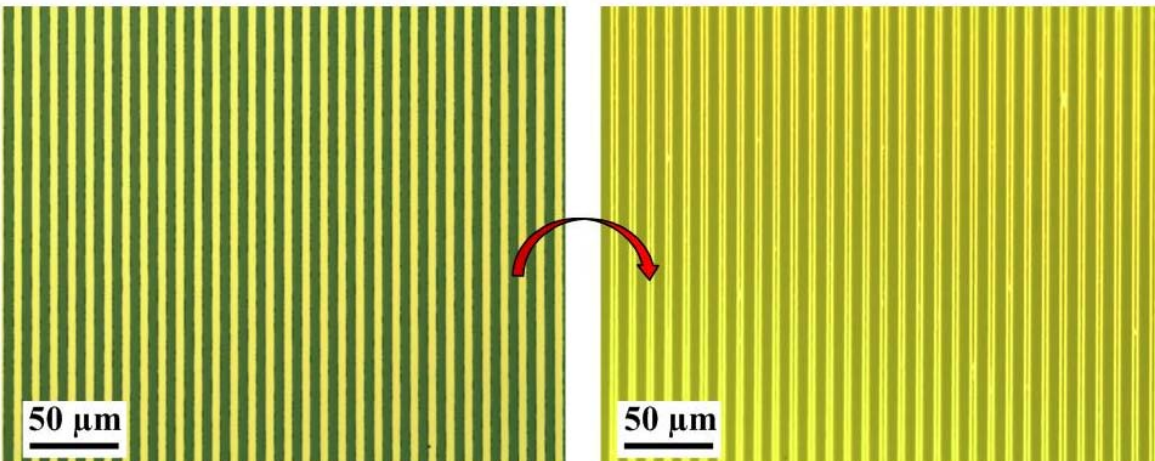
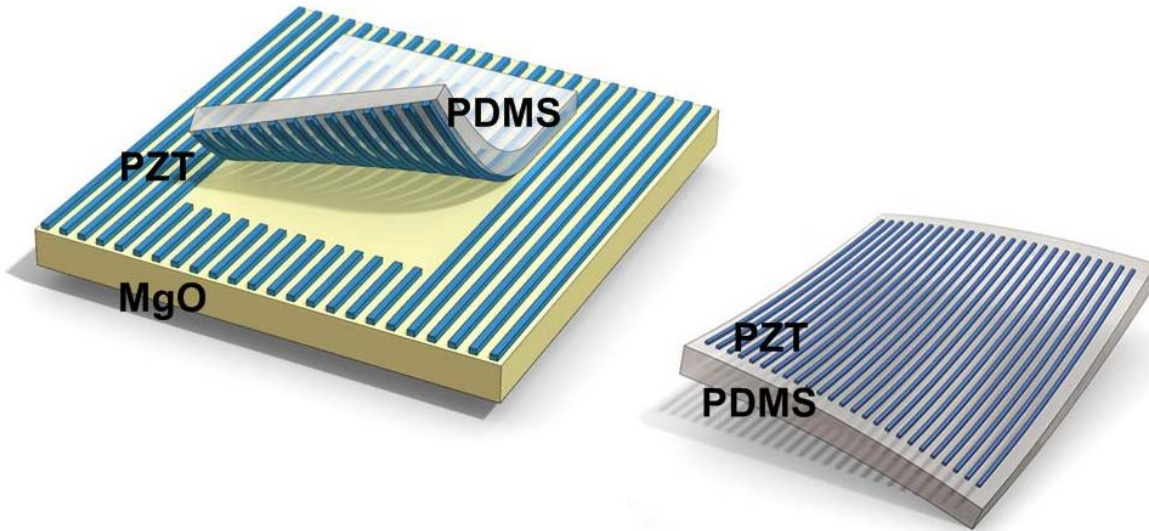
—100  $\mu\text{m}$ —



# PZT NWs

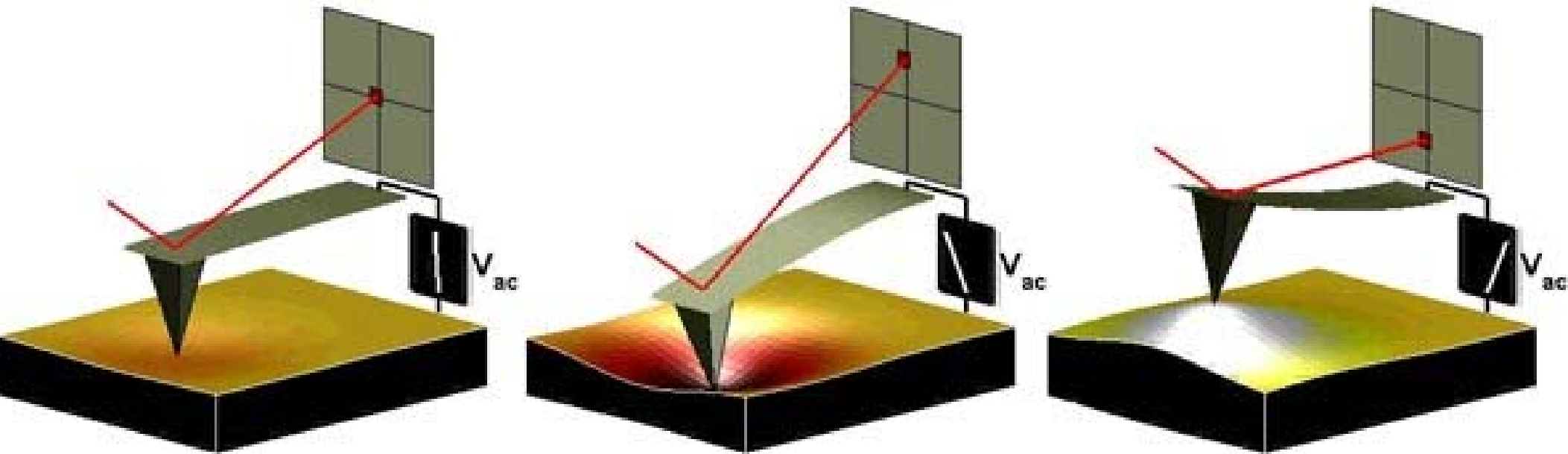


# Printing



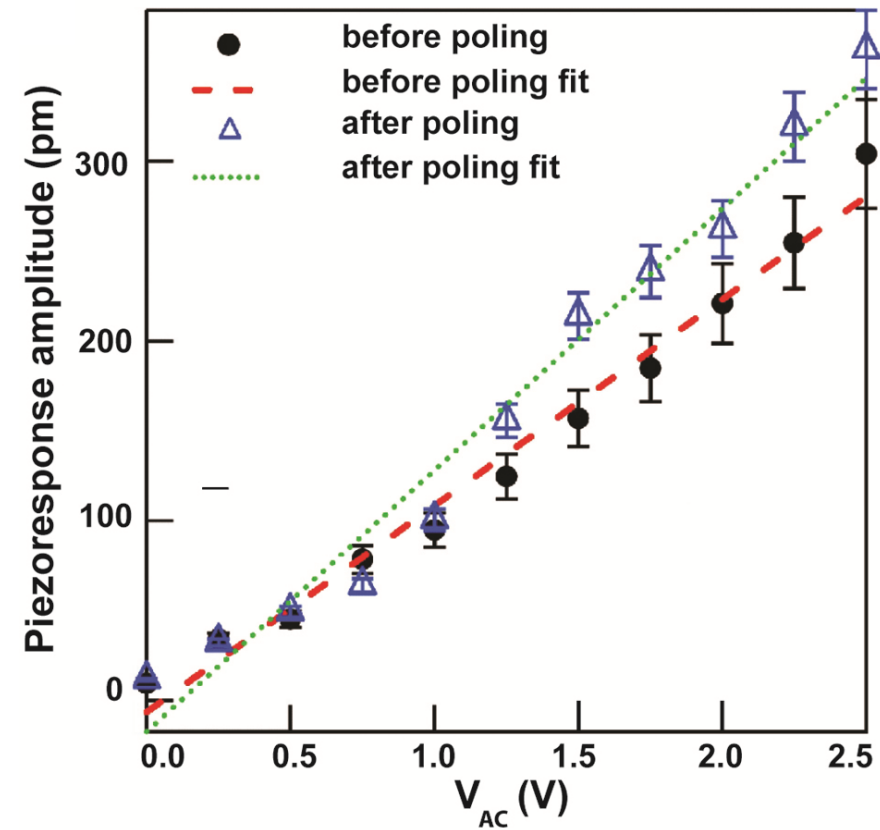
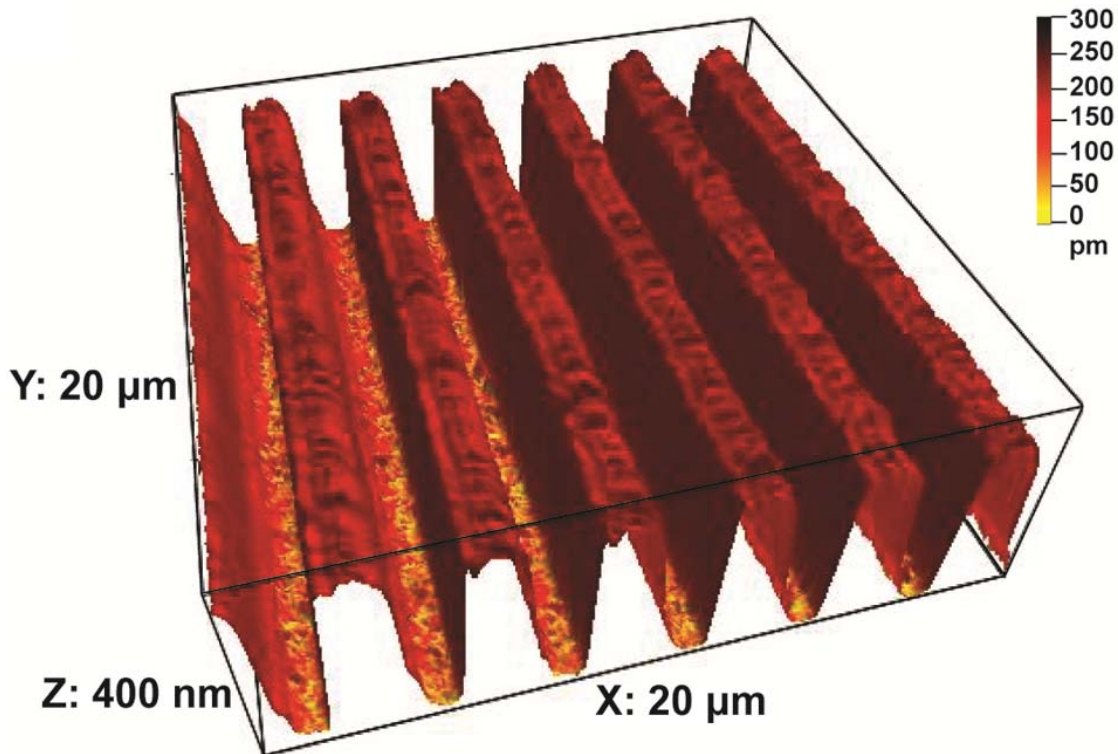


# Piezoforce Microscopy



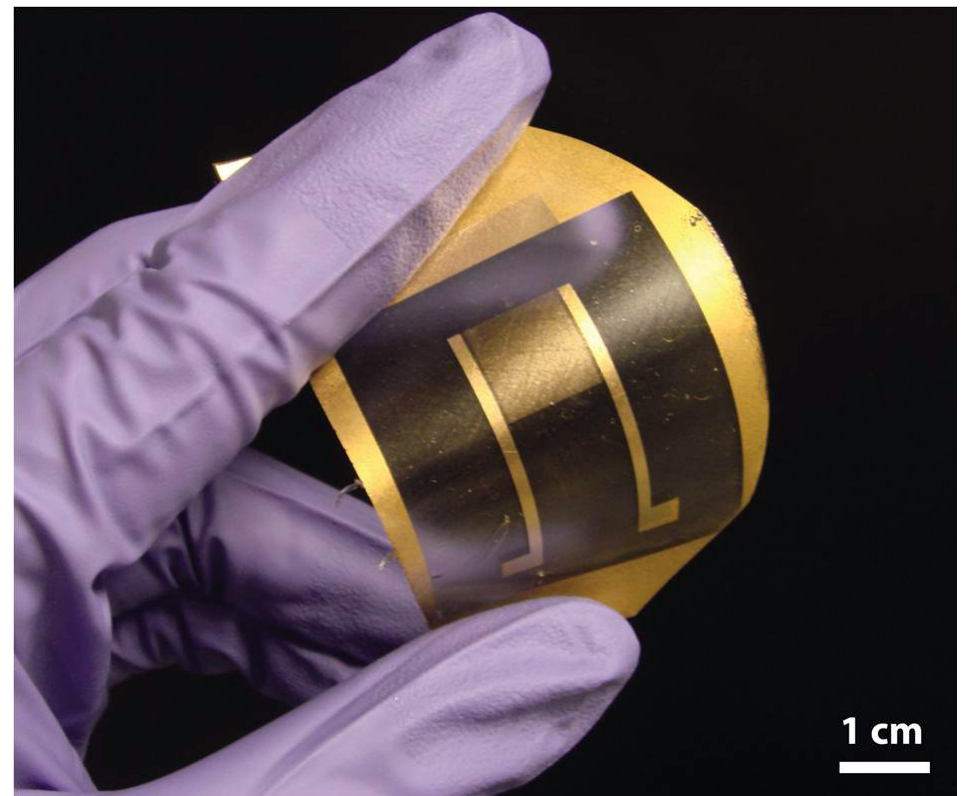
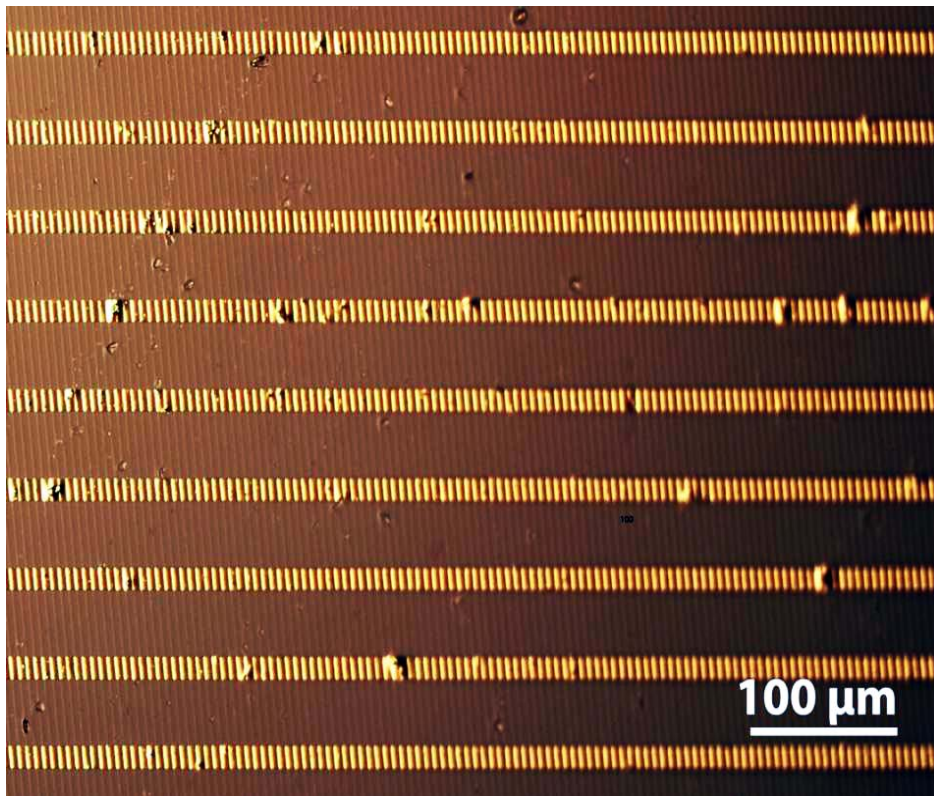
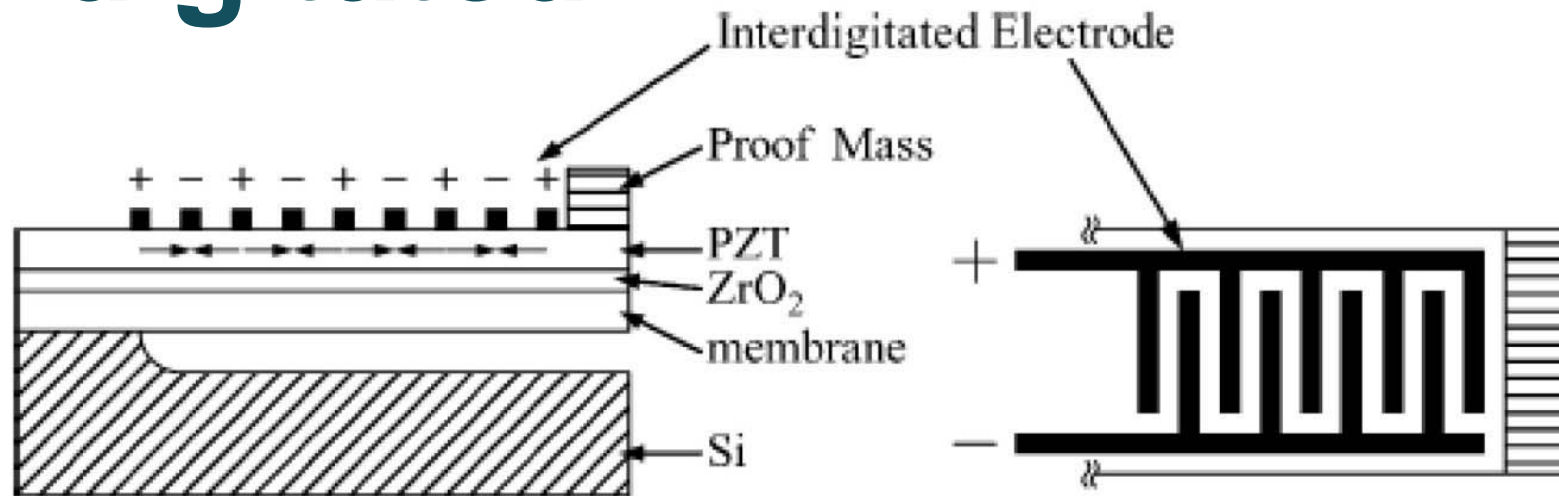
$$d_{\text{eff}} = A_{\text{VIB}}/V_{\text{AC}}$$

# PFM

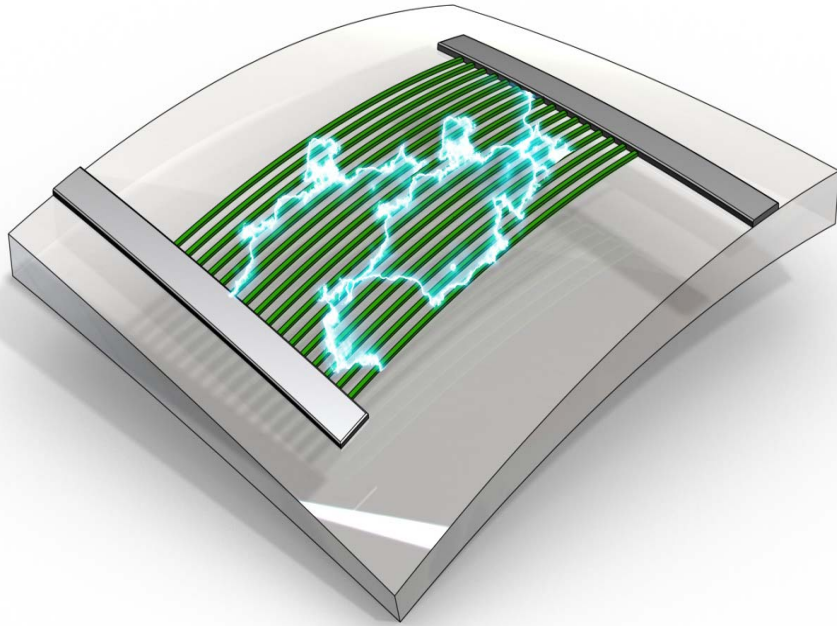


$$d_{33} = 100 \text{ pm/V}$$

# Interdigitated

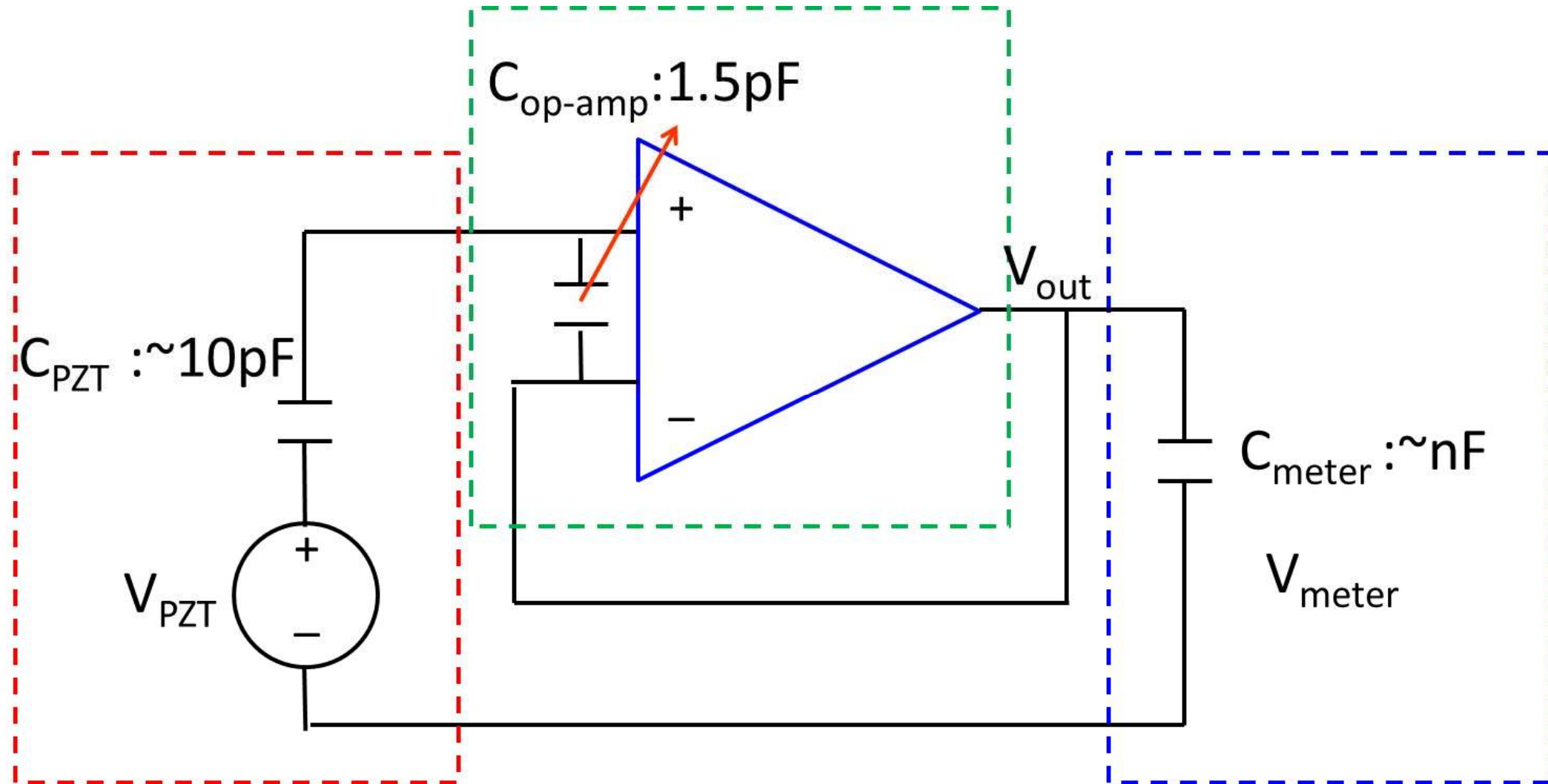


# Prototype



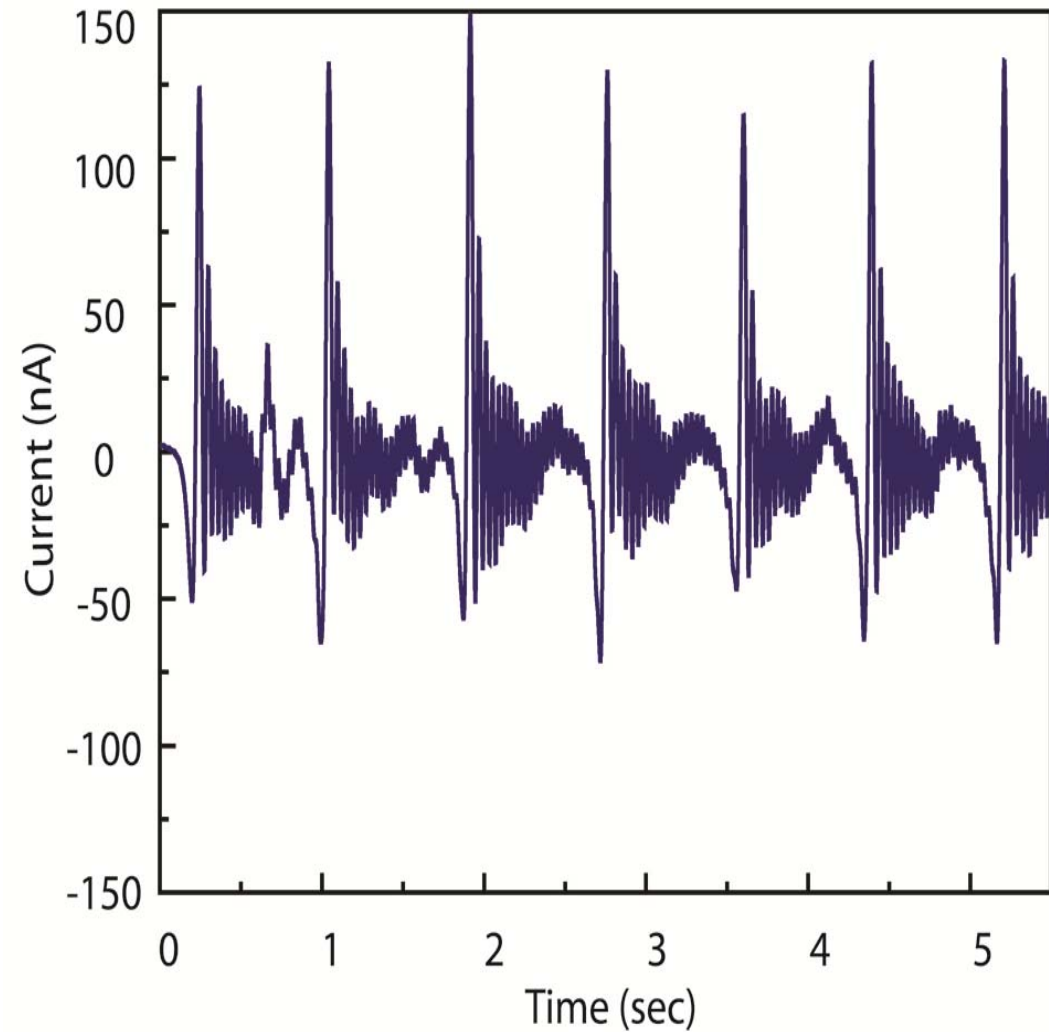
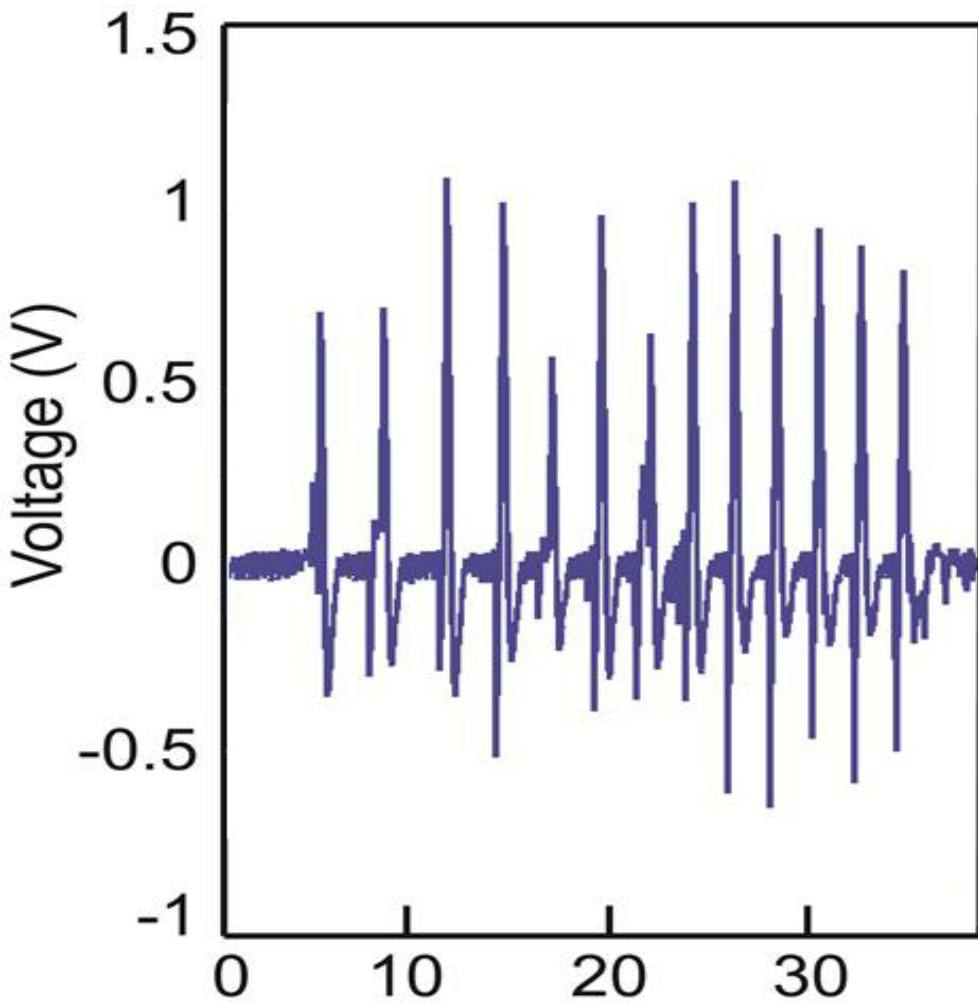


# Impedance Matching





# Power

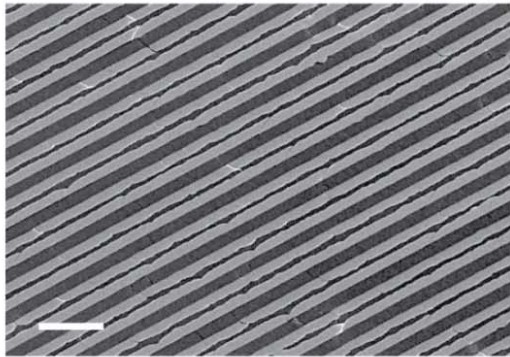


**Power = 10 mW/cm<sup>3</sup>**

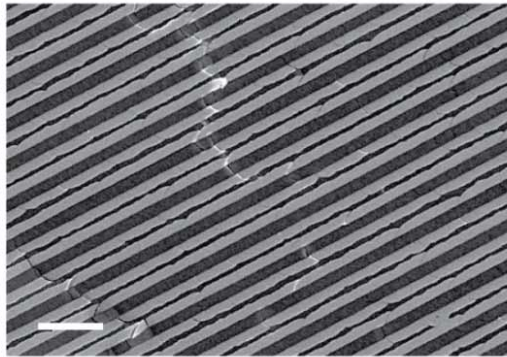
# Comparison

|   |  |
|---|--|
| <b>This work</b><br><b>Printed PZT Nanoribbons</b>  | <b>Voltage: 1.5 V</b><br><b>Current: 200 nA</b><br><b>Power: 0.3 <math>\mu</math>W</b><br><b>Power Density: 10 mW/cm<sup>3</sup></b> |
| <b>Chen, Xu, Yao, Shi</b><br><b>PZT Nanofibers</b><br><b>Nano Letters</b><br><b>10.1021/nl100812k</b>             | <b>Voltage: 1.63 V</b><br><b>Current: 20 nA</b><br><b>Power: 30 nW</b><br><b>Power Density: Unknown</b>                              |
| <b>Xu, Hansen, Wang</b><br><b>PZT Nanowire Arrays</b><br><b>Nature Communications</b><br><b>10.1038/ncomms109</b> | <b>Voltage: 0.7 V</b><br><b>Current: 100 nA</b><br><b>Power: 100 nW</b><br><b>Power Density: 2.8 mW/cm<sup>3</sup></b>               |

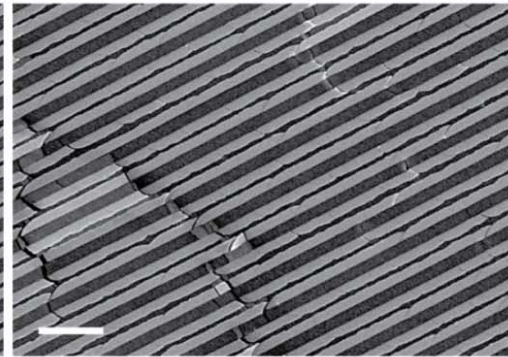
# Failure



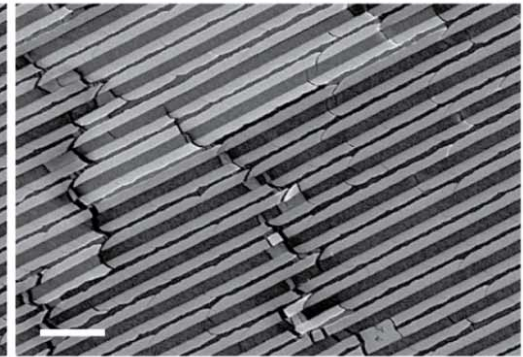
$s = 0\%$



$s = 1.5\%$



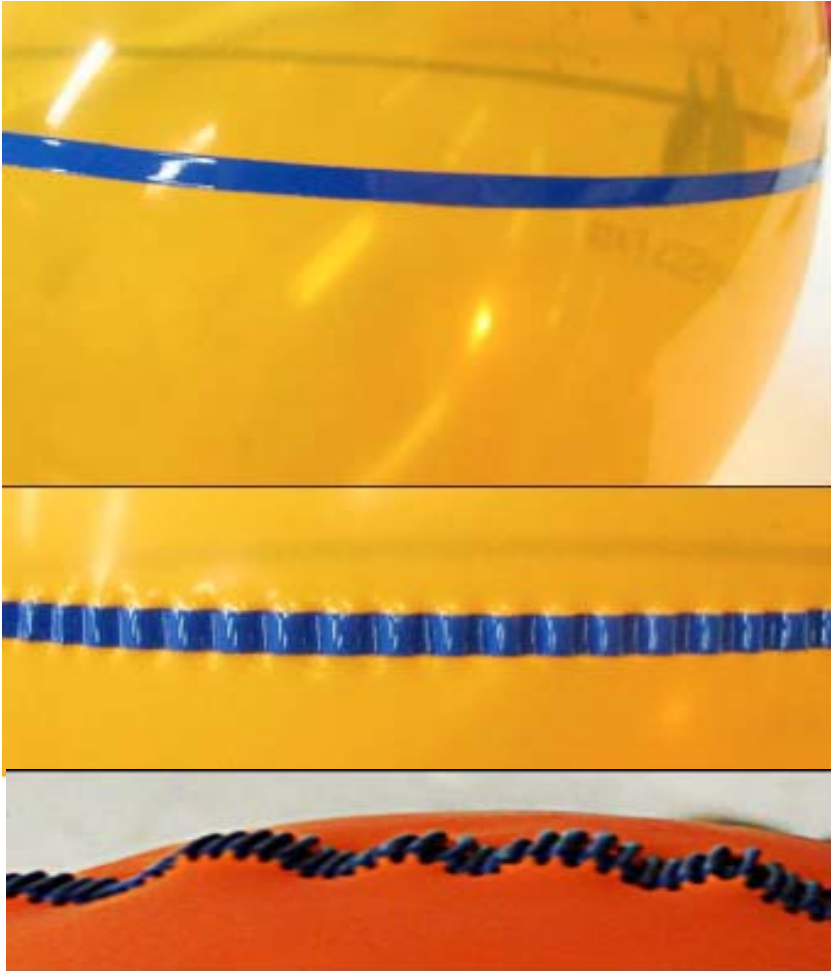
$s = 3.0\%$



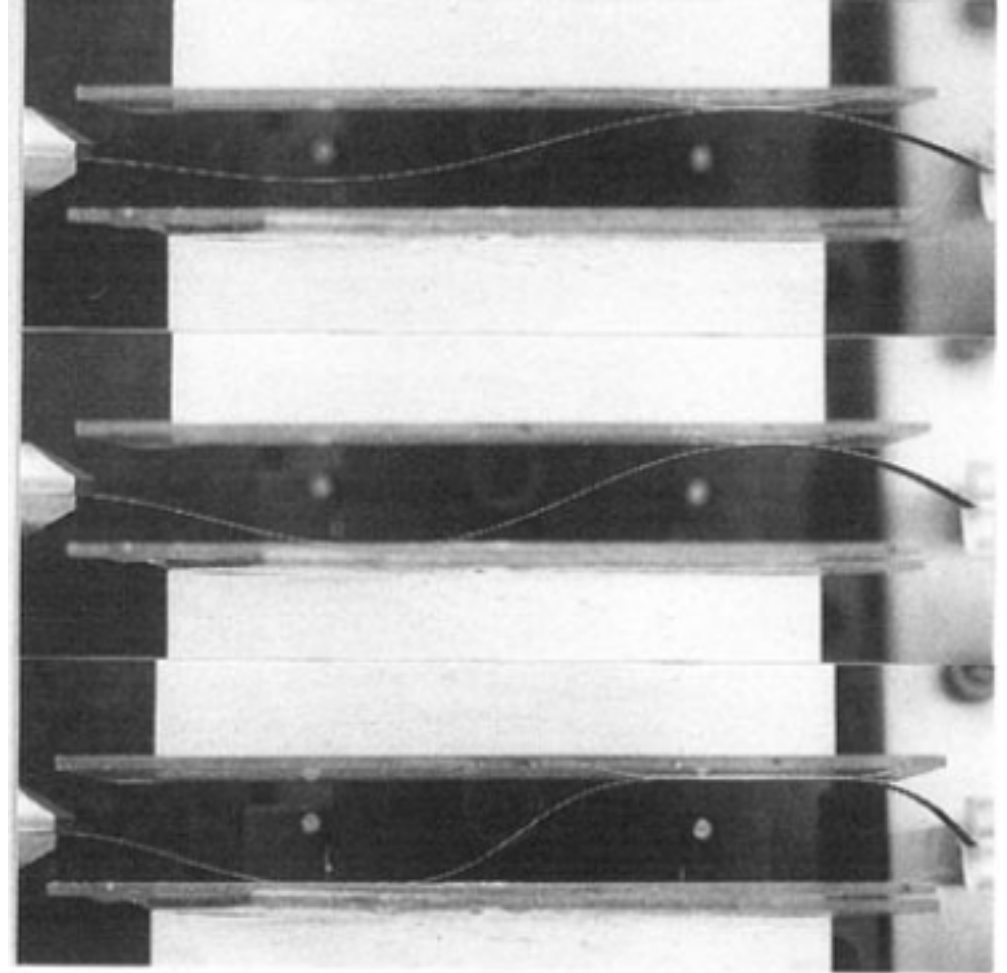
$s = 4.5\%$



# Buckling



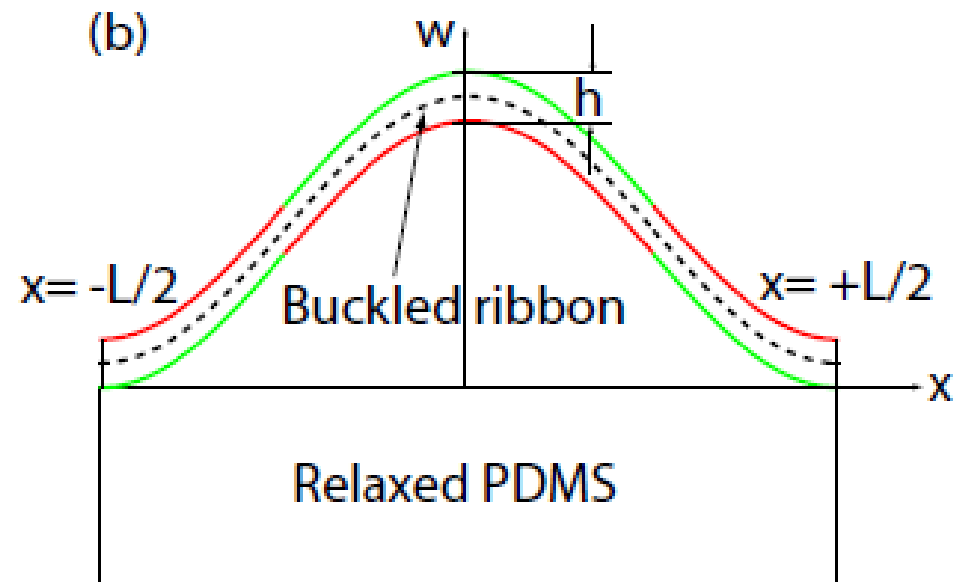
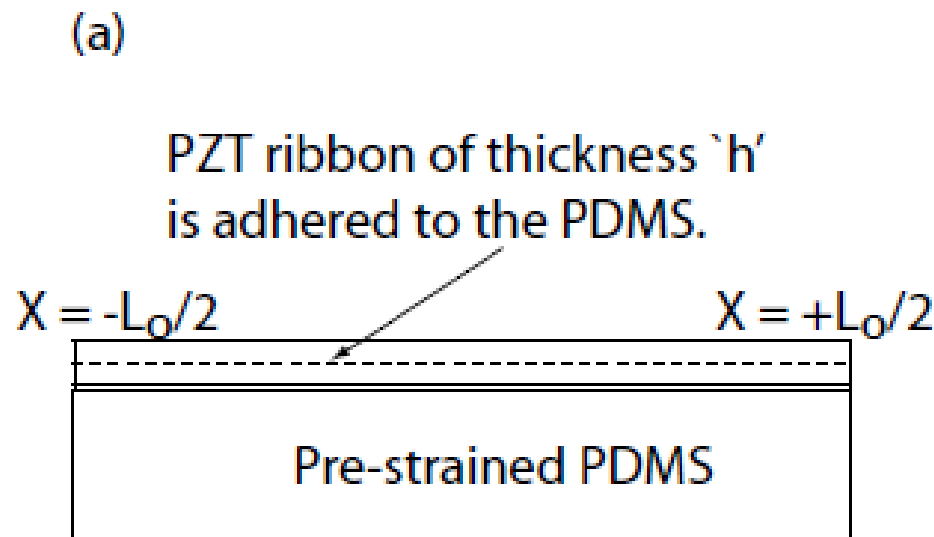
A. Concha, J. W. Merver III, P. Mellado, D. Clarke, O. Tchernyshyov, R. L. Leheny, *Phys Rev E* 75, 016609 (2007)



G. Domokos, P. Holmes, B. Royce, *J Nonlinear Sci* 7, 281-314 (1997)



# Parameters



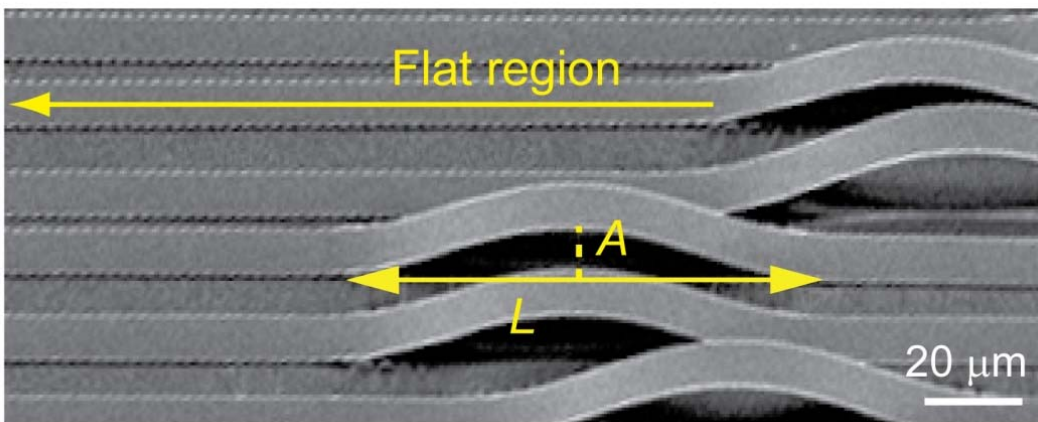
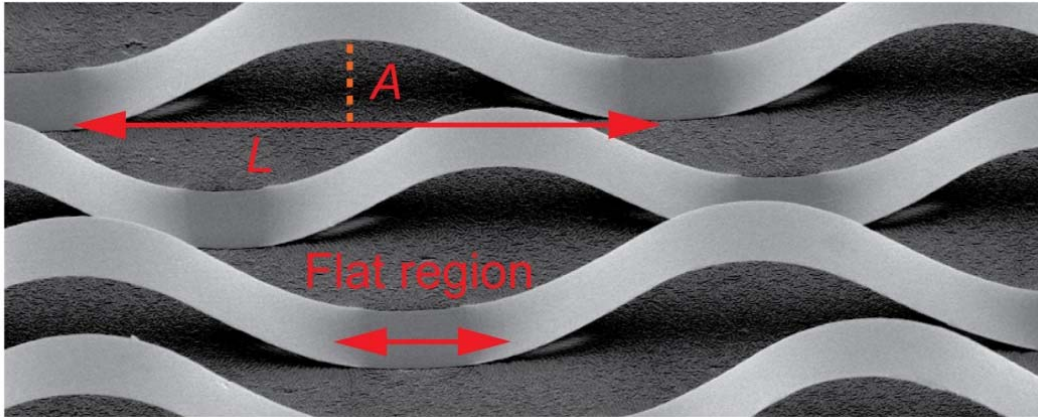
$$U^{bend} = \int_{-\frac{L_0}{2}}^{+\frac{L_0}{2}} \frac{1}{2} \frac{Eh^3}{12} \left( \frac{d^2w}{dX^2} \right)^2 dX = \frac{Eh^3}{12} \frac{\pi^4 A^2}{L_0^3},$$

$$U^{mid} = \int_{-\frac{L_0}{2}}^{+\frac{L_0}{2}} \frac{1}{2} Eh \epsilon_{mid}^2 dX = \frac{1}{2} EhL_0 \left( \frac{\pi^2 A^2}{4L_0^2} - \frac{\epsilon_{pre}}{1 + \epsilon_{pre}} \right)^2$$

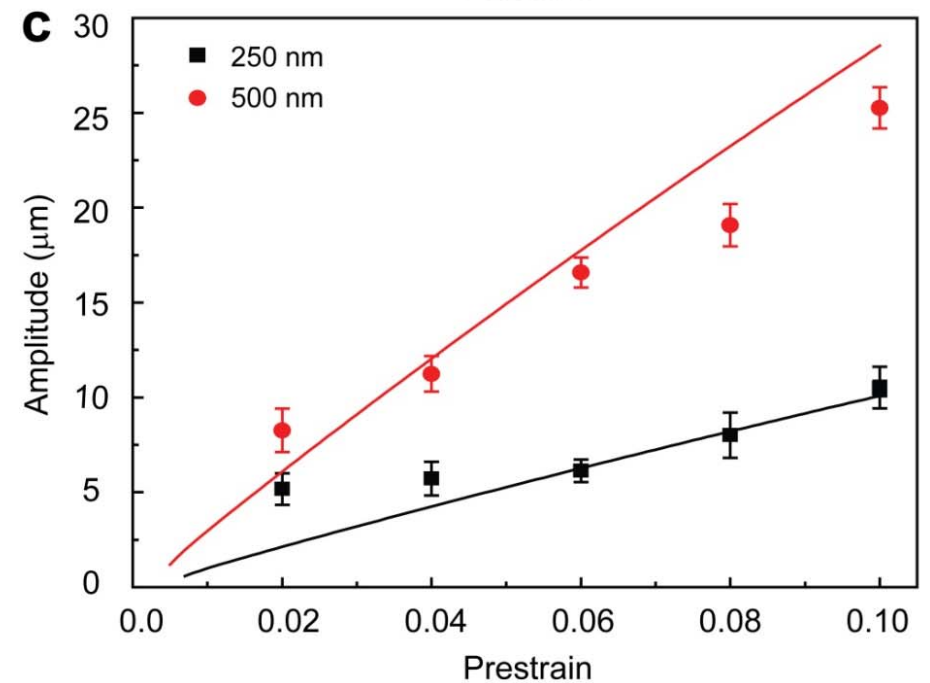
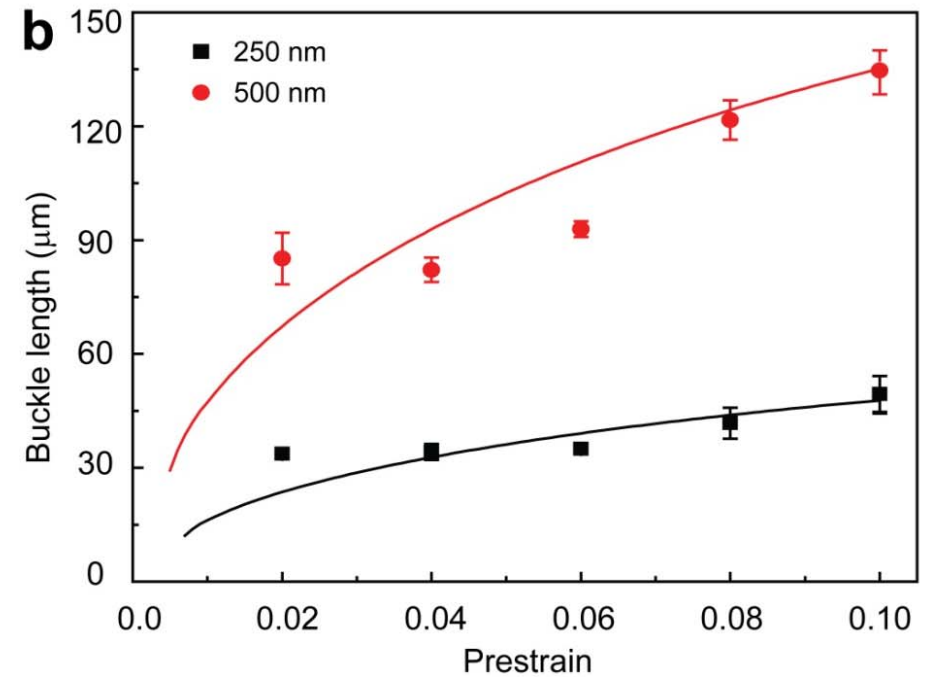
$$U^{adh} = W_{ad}L_0.$$

# Waveforms

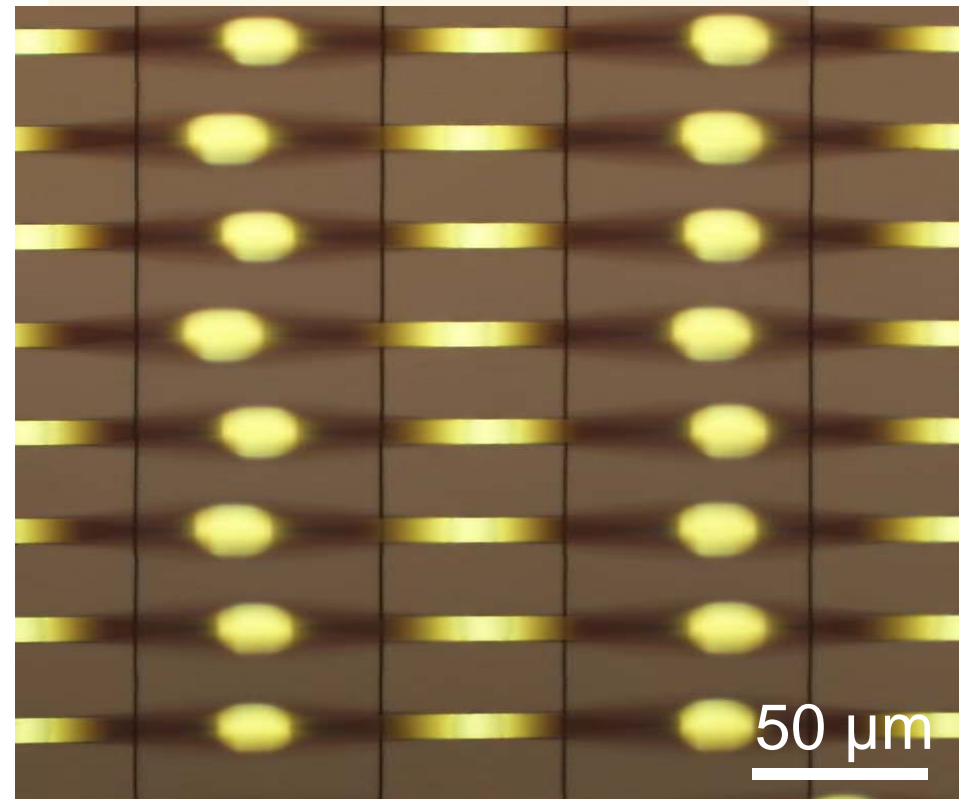
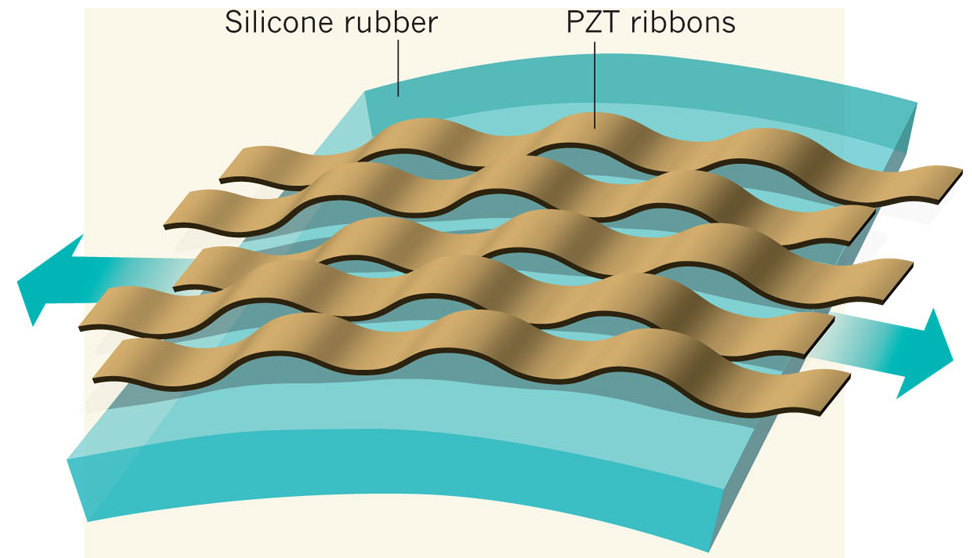
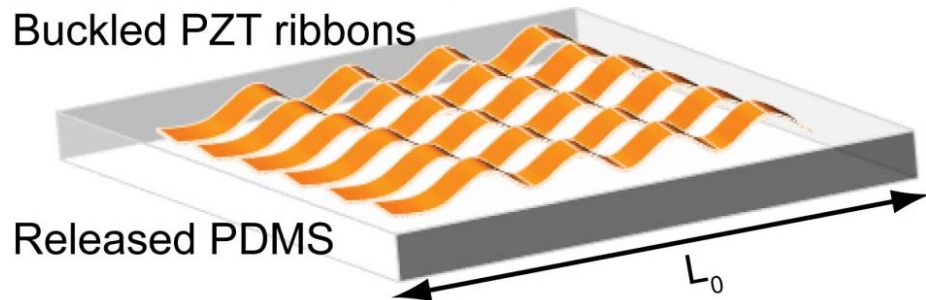
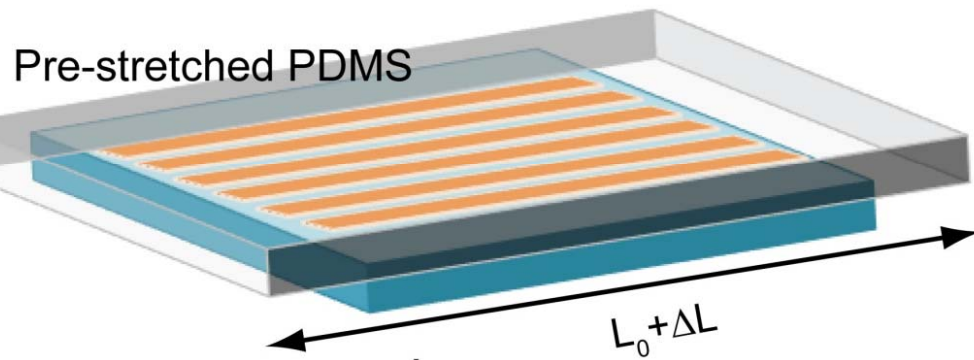
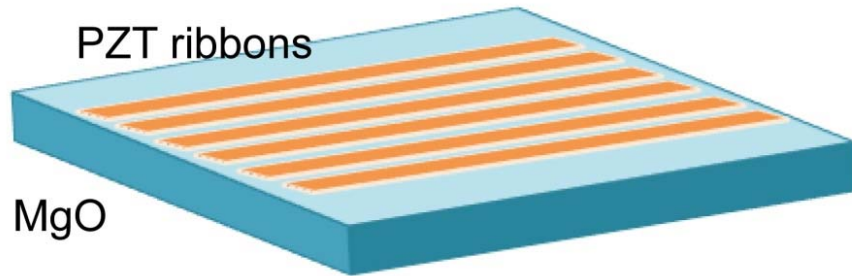
8% Prestrain



2% Prestrain

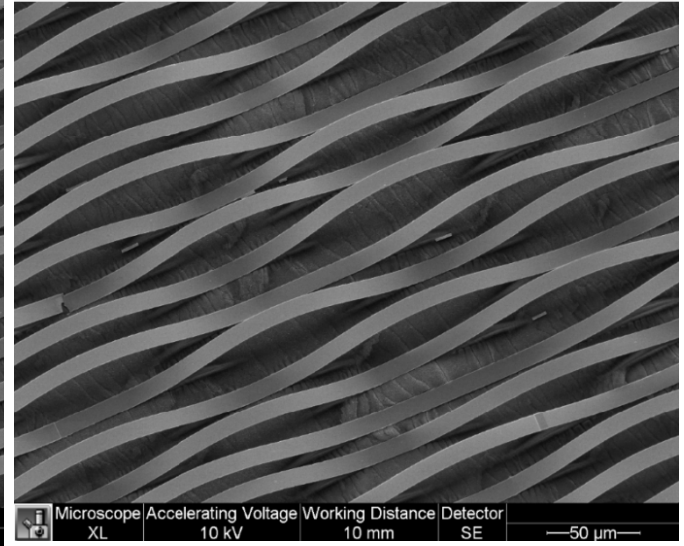
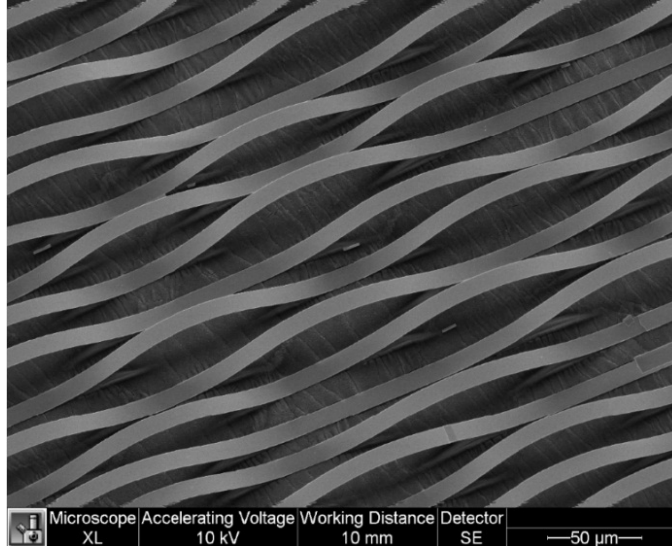
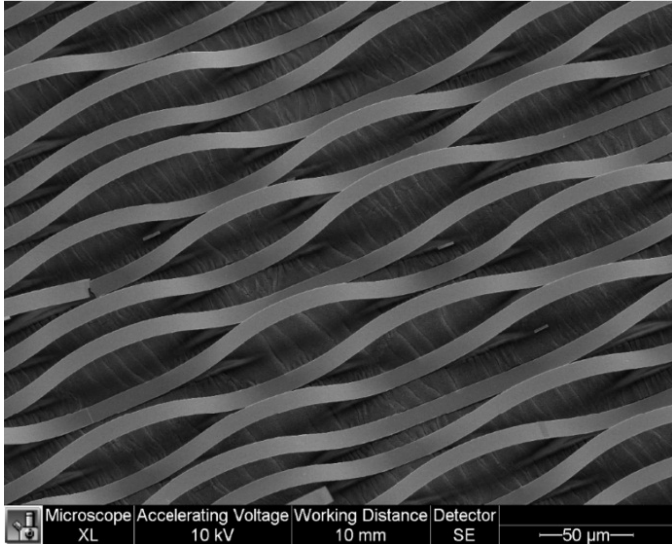


# Buckled PZT



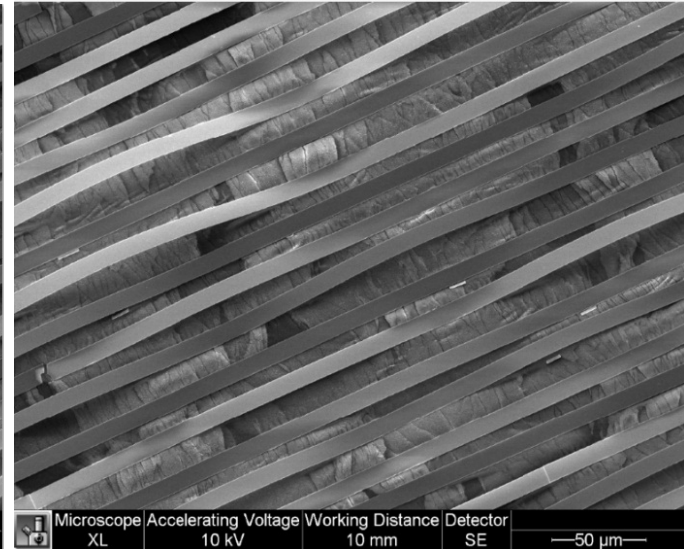
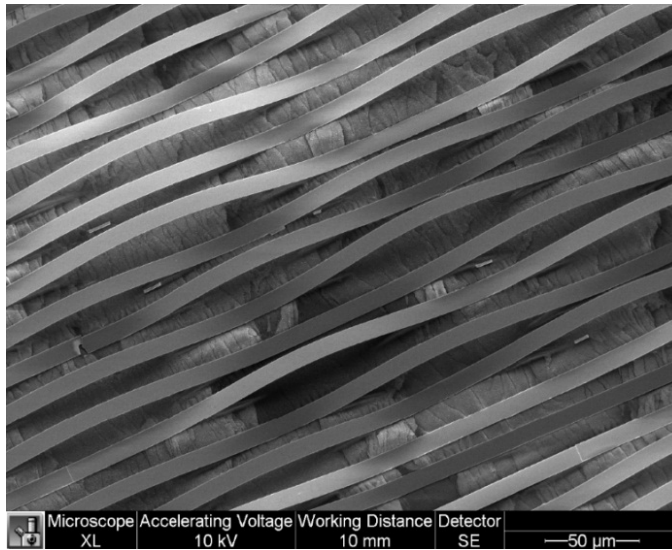
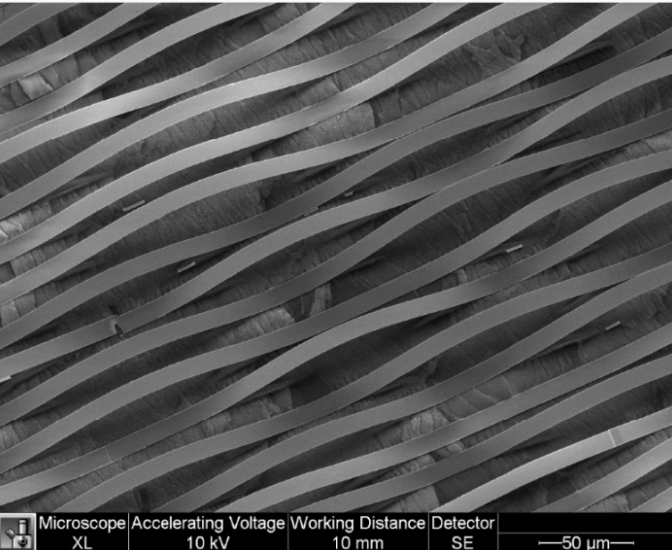


# Stretchability



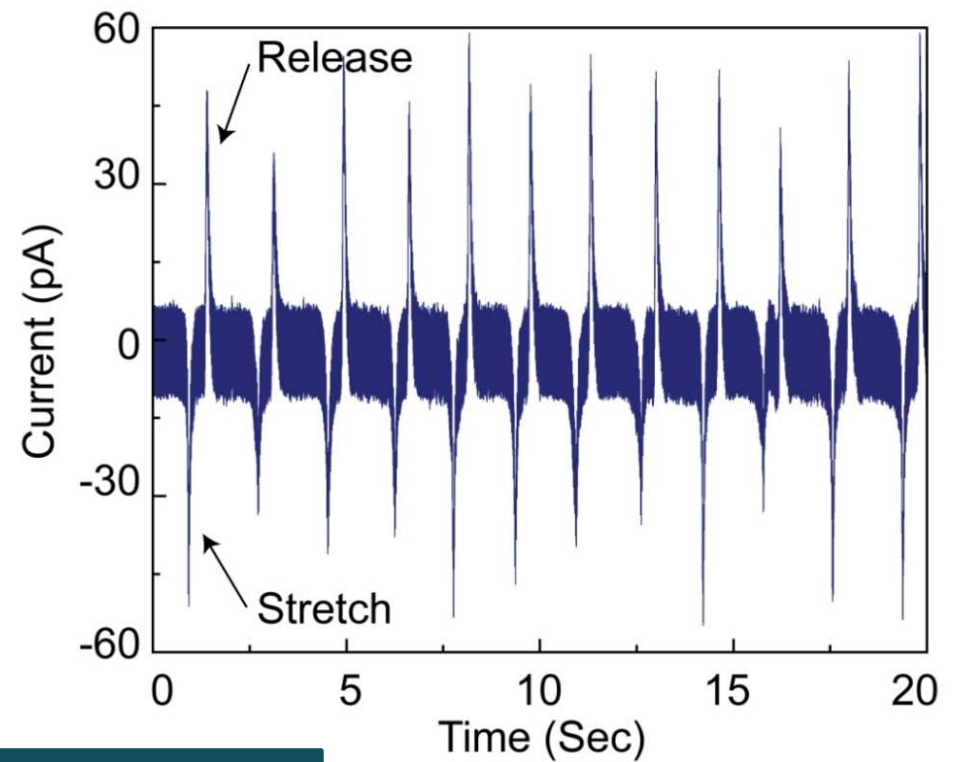
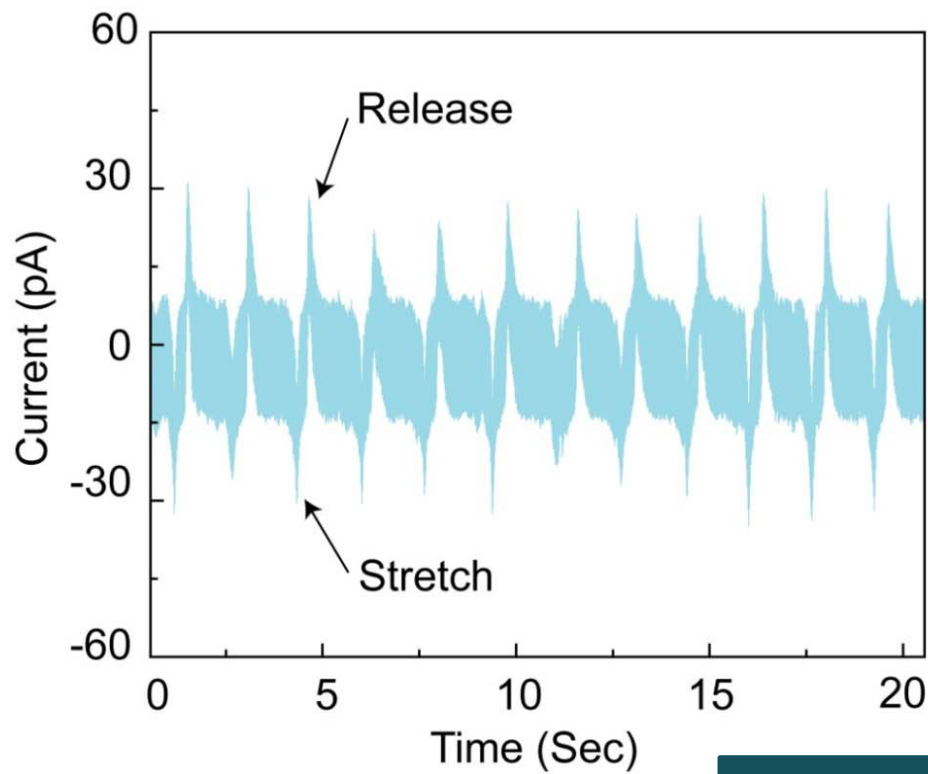
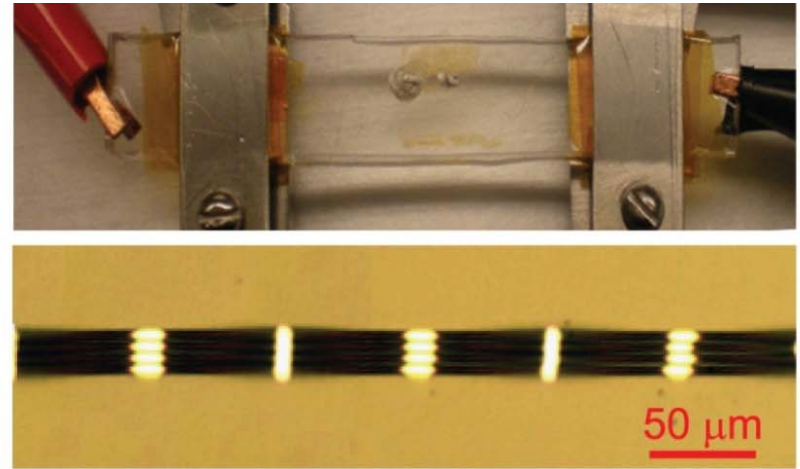
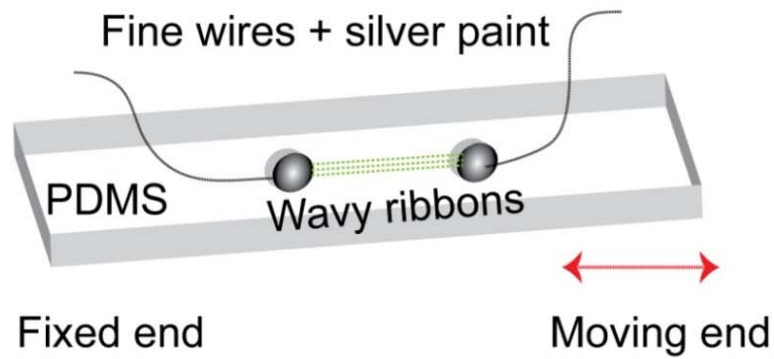
0%

10%





# Generator



**$0.25\ \text{mA}/\text{cm}^2$**

# Science and Nature

## Nanogenerators Tap Waste Energy To Power Ultrasmall Electronics

Tiny devices that convert movements into electricity won't power cities. But they may soon be efficient enough to power arrays of invisible sensors and hand-held electronics

—ROBERT F. SERVICE

[www.sciencemag.org](http://www.sciencemag.org) SCIENCE VOL 328 16 APRIL 2010

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## Power surfing on waves

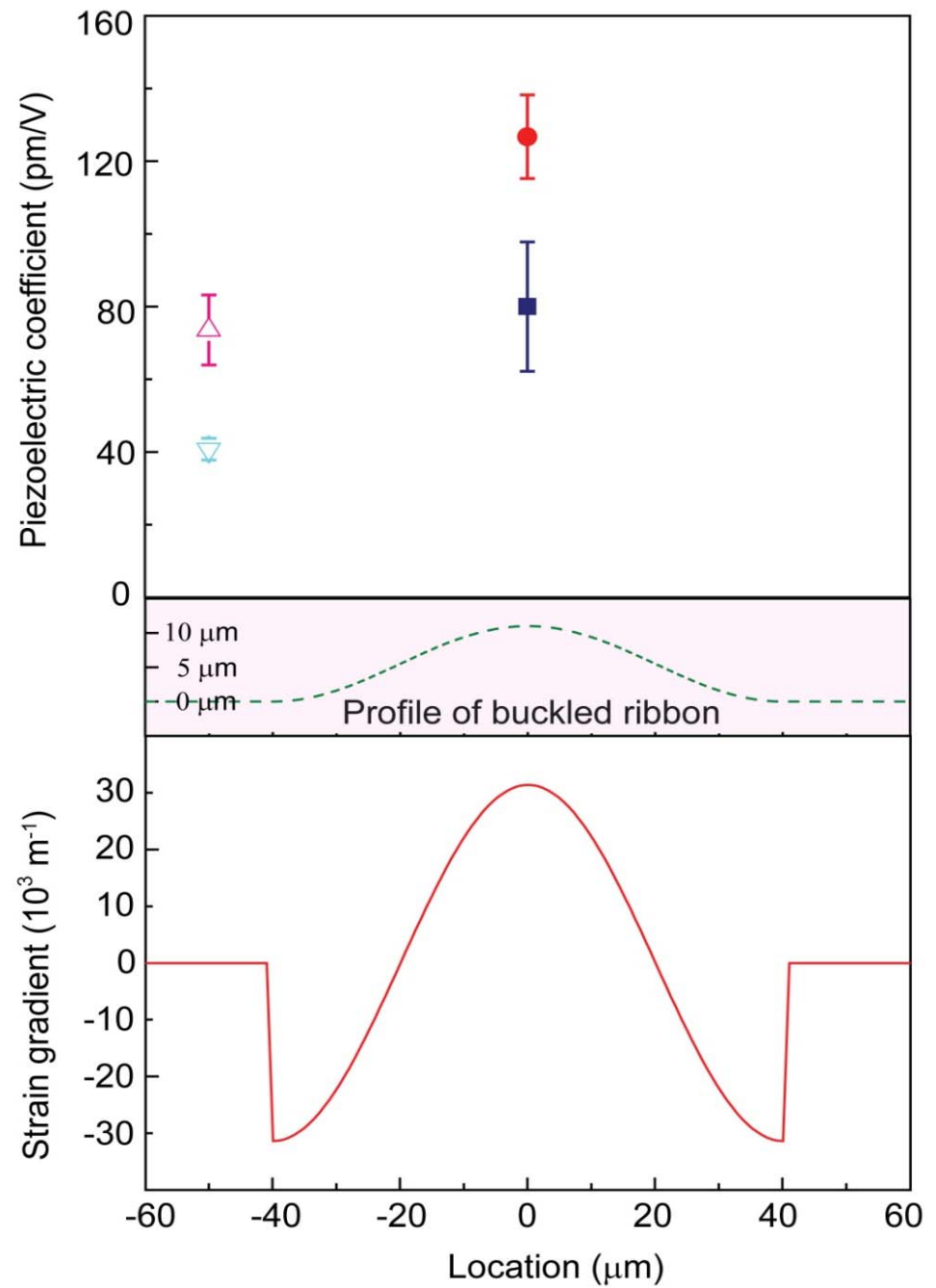
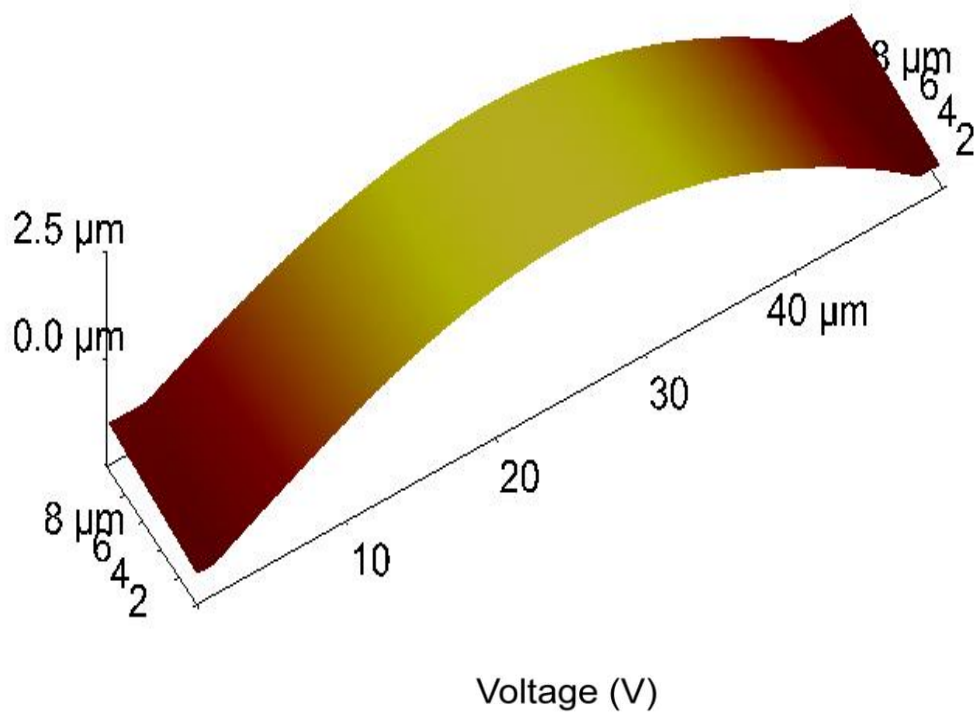
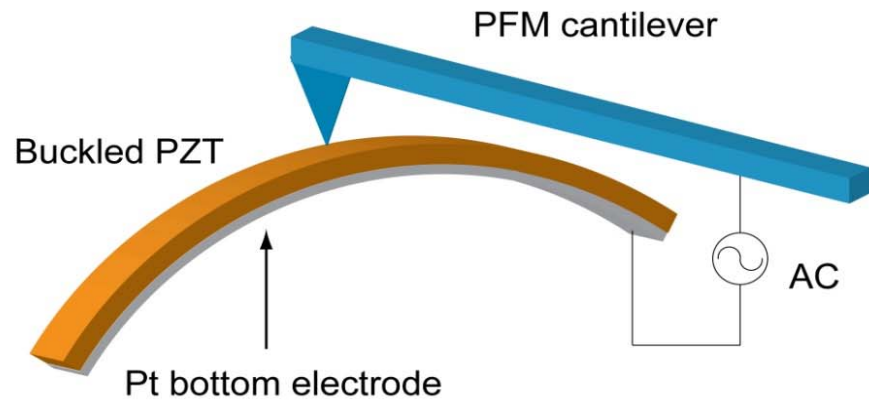
Wavy strips of piezoelectric materials on stretchable substrates can both withstand larger applied mechanical strain without cracking and harvest energy more efficiently than their flat counterparts.

MIN HYUNG LEE & ALI JAVEY

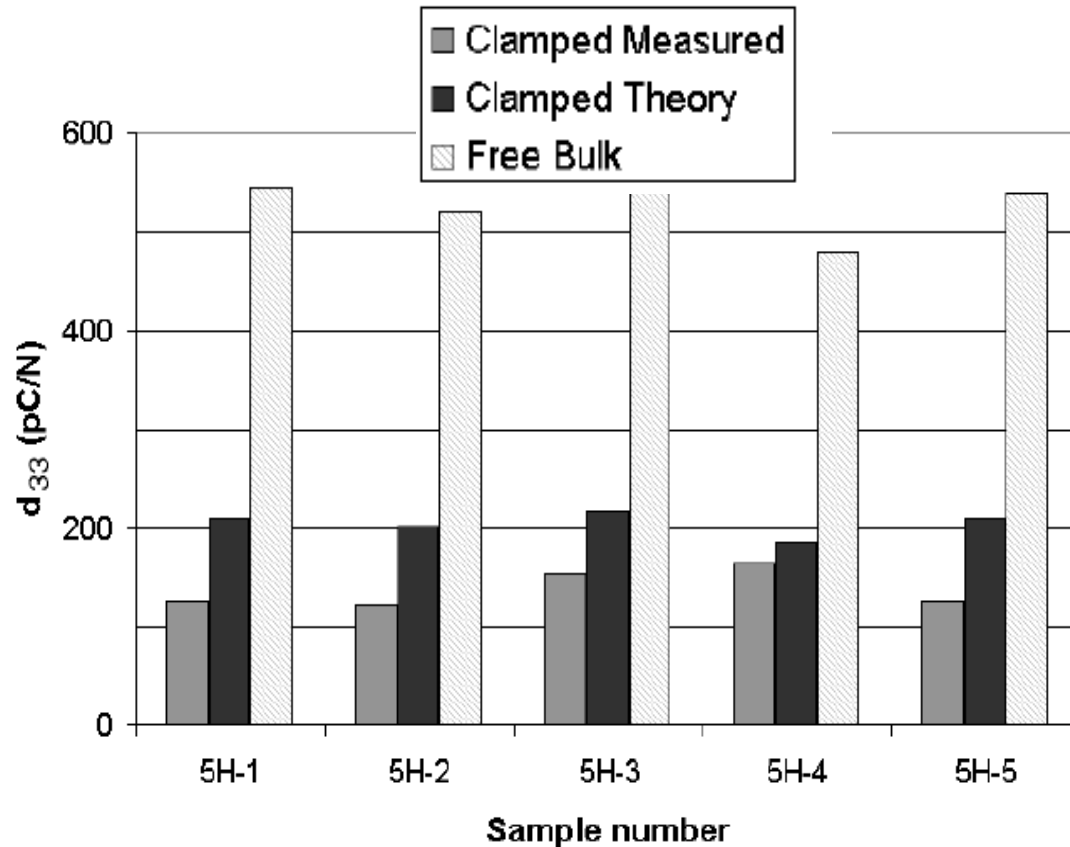
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304 | NATURE | VOL 472 | 21 APRIL 2011

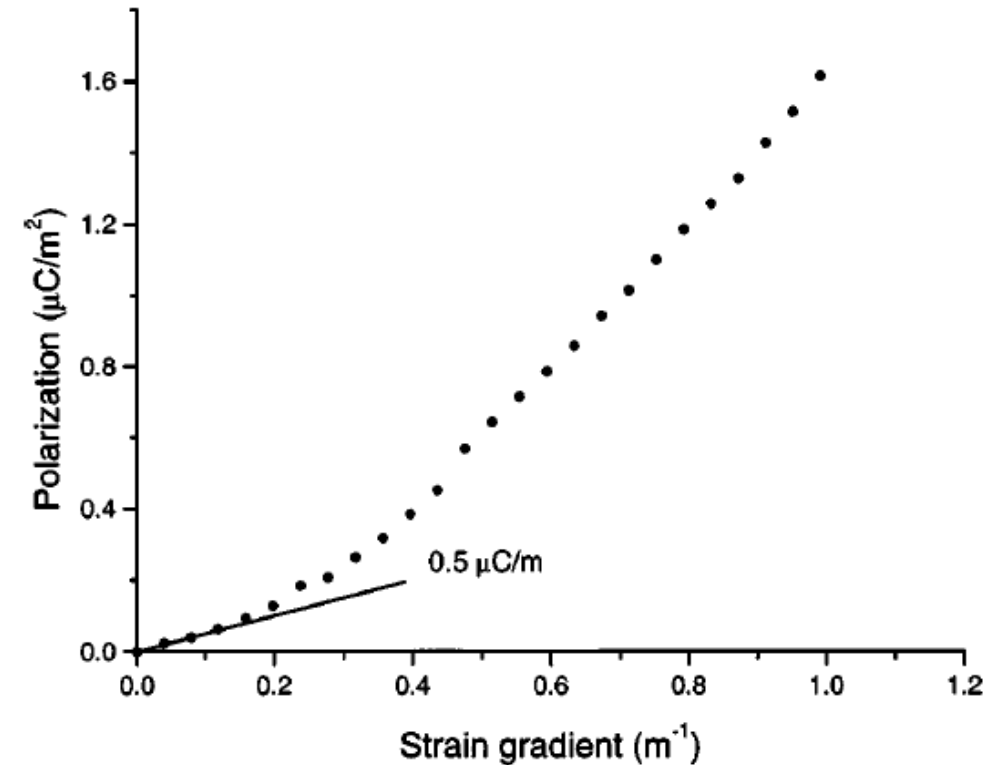
# Local Probing



# Enhancement



Torah, Beeby, White, *J Phys D* 37, 1 (2004)

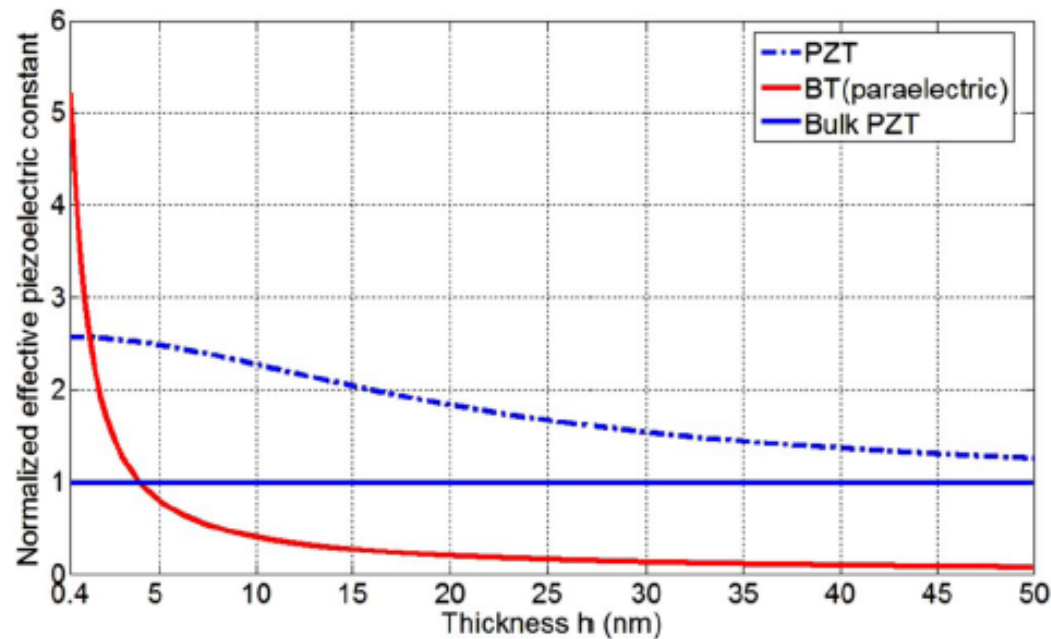
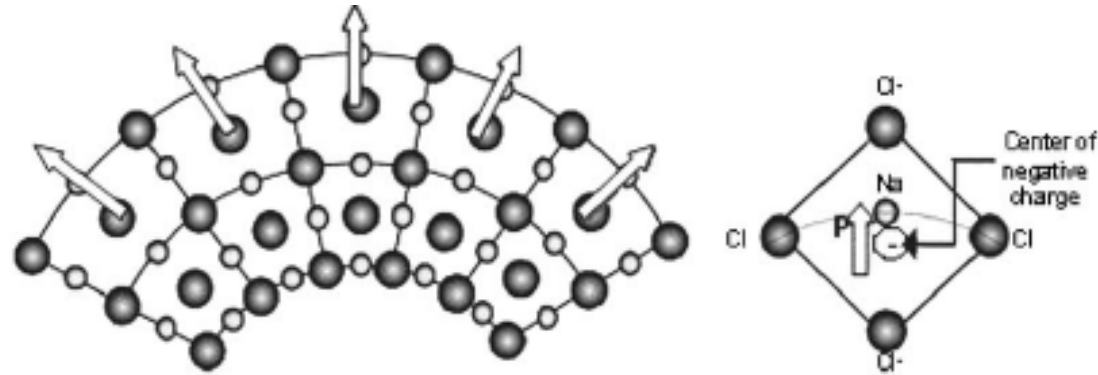


W. H. Ma, L. E. Cross, *Appl Phys Lett* 82, 3293 (2003)



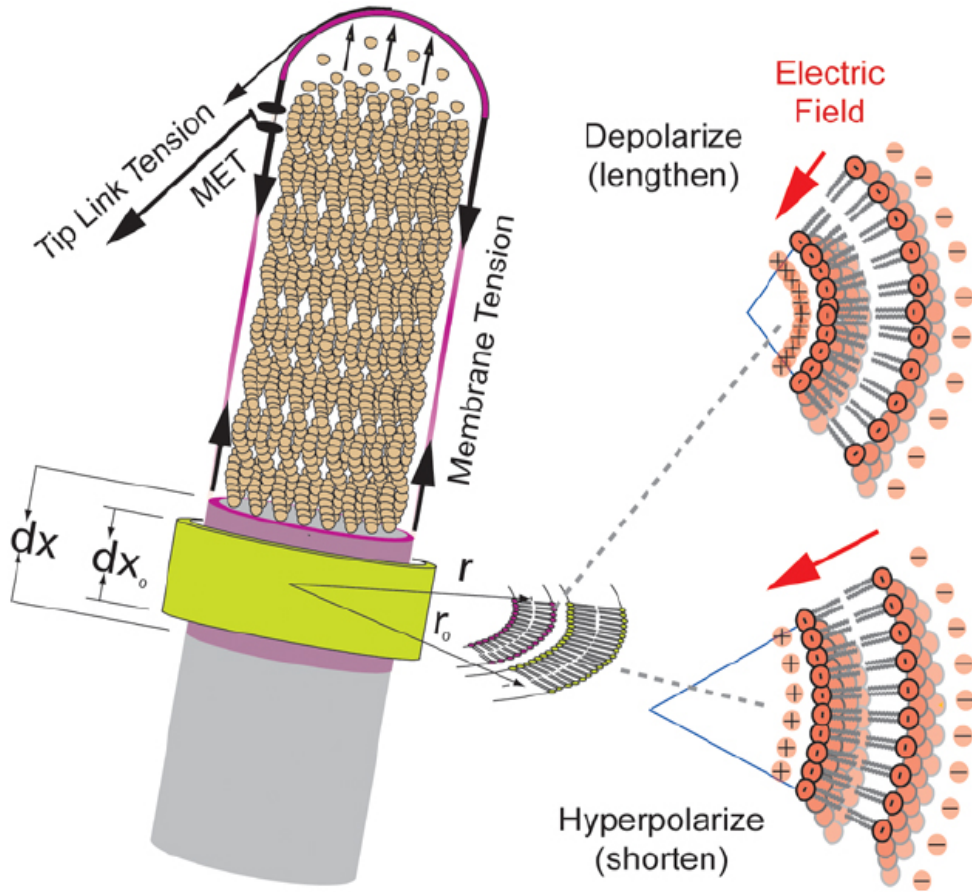
# Flexoelectricity

$$(\mathbf{P})_i = (\mathbf{d})_{ijk} (\boldsymbol{\varepsilon})_{jk} + (\mathbf{f})_{ijkl} \nabla_l (\boldsymbol{\varepsilon})_{jk}$$

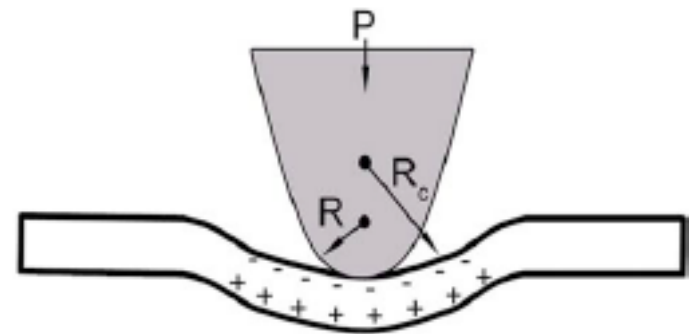
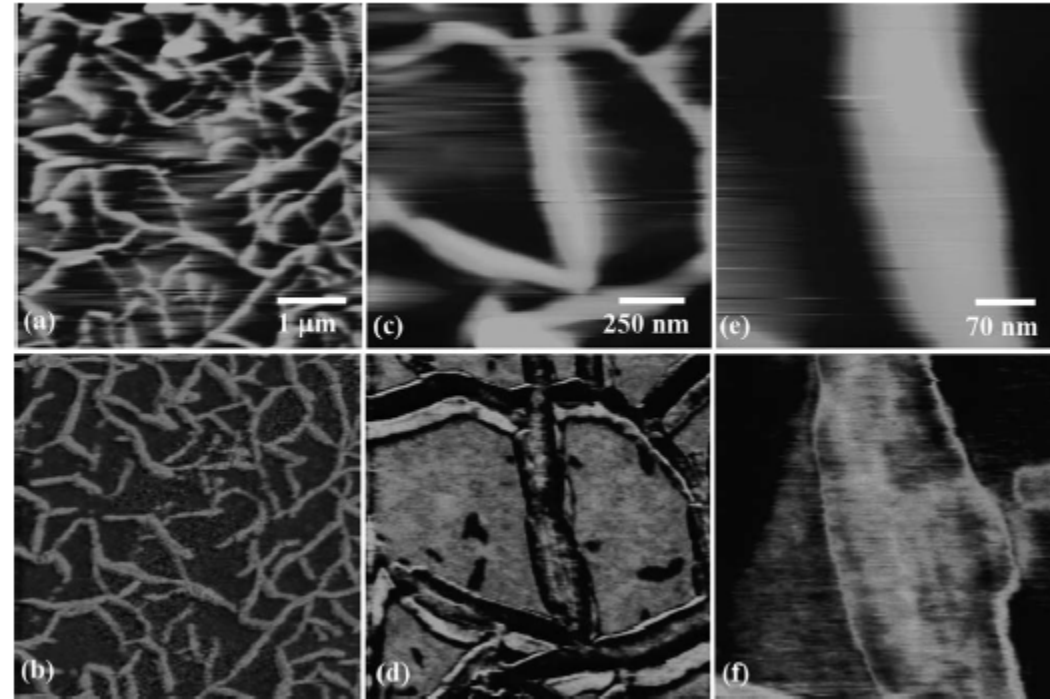


Maranganti, Sharma, Sharma, *Phys Rev B* 74, 014110 (2006)

# Soft Matter

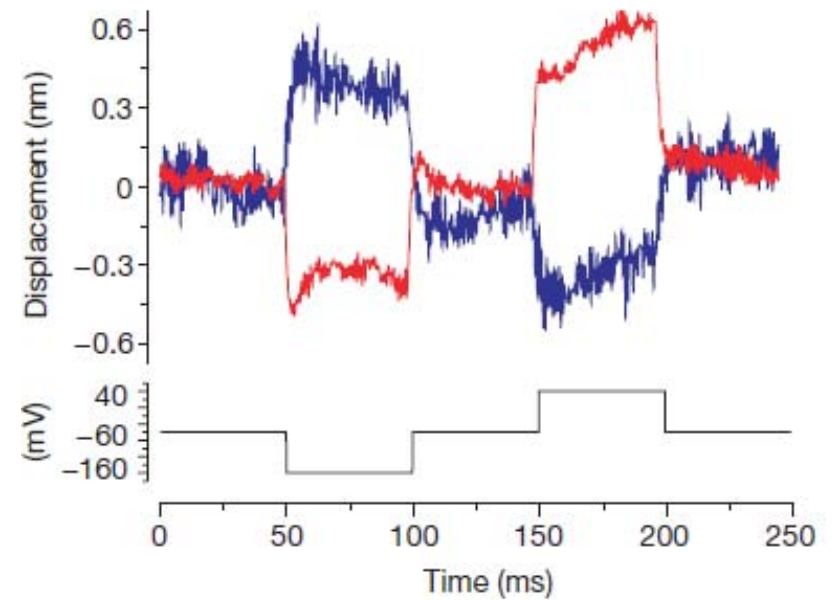
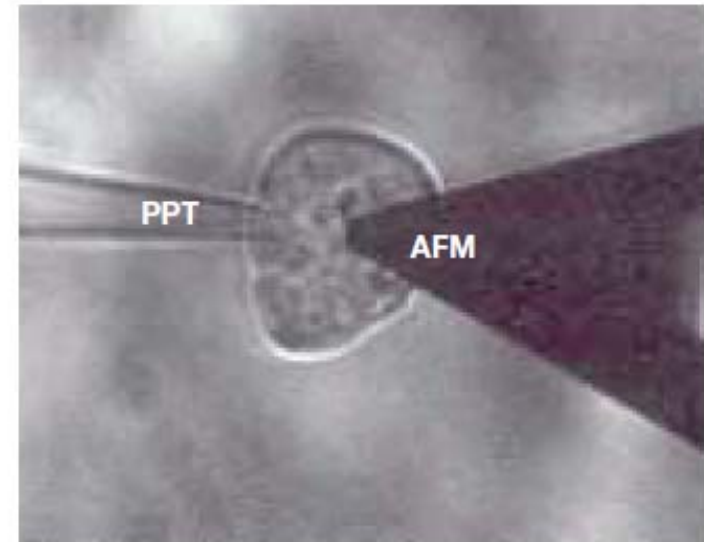
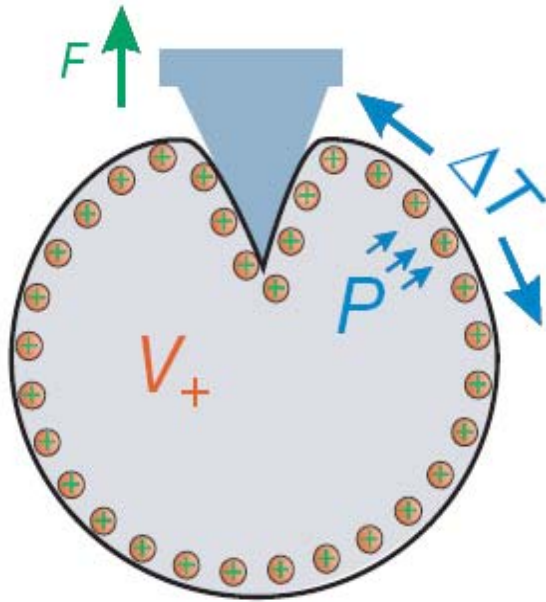


K. D. Breneman, W. E. Brownell, R. D. Rabbitt, *PLoS One* 4, e5201 (2009)



Kalinin, Jesse, Liu, Balandin, *Appl Phys Lett* 88, 153902 (2006)

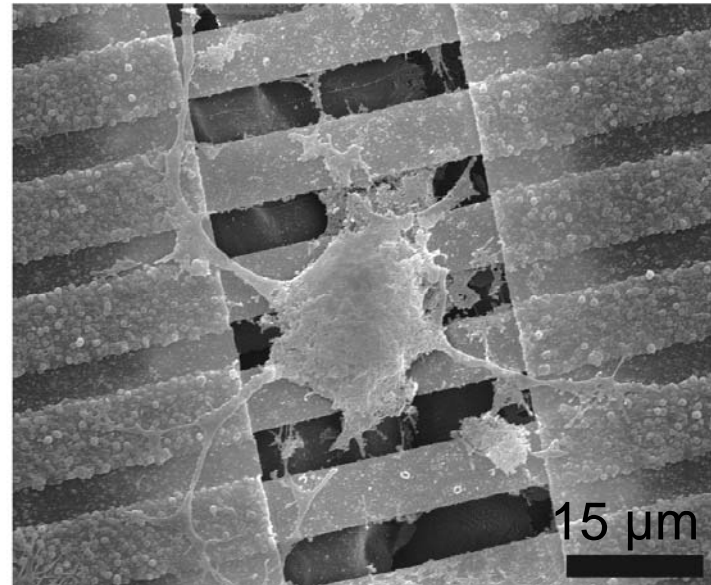
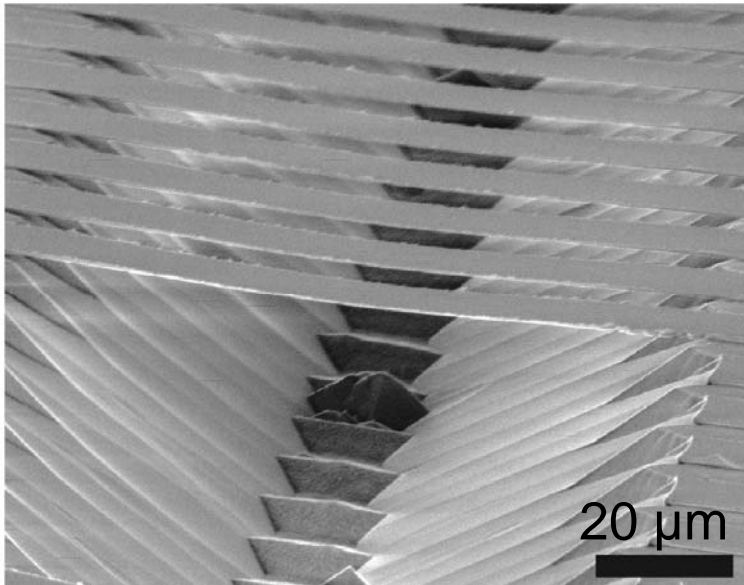
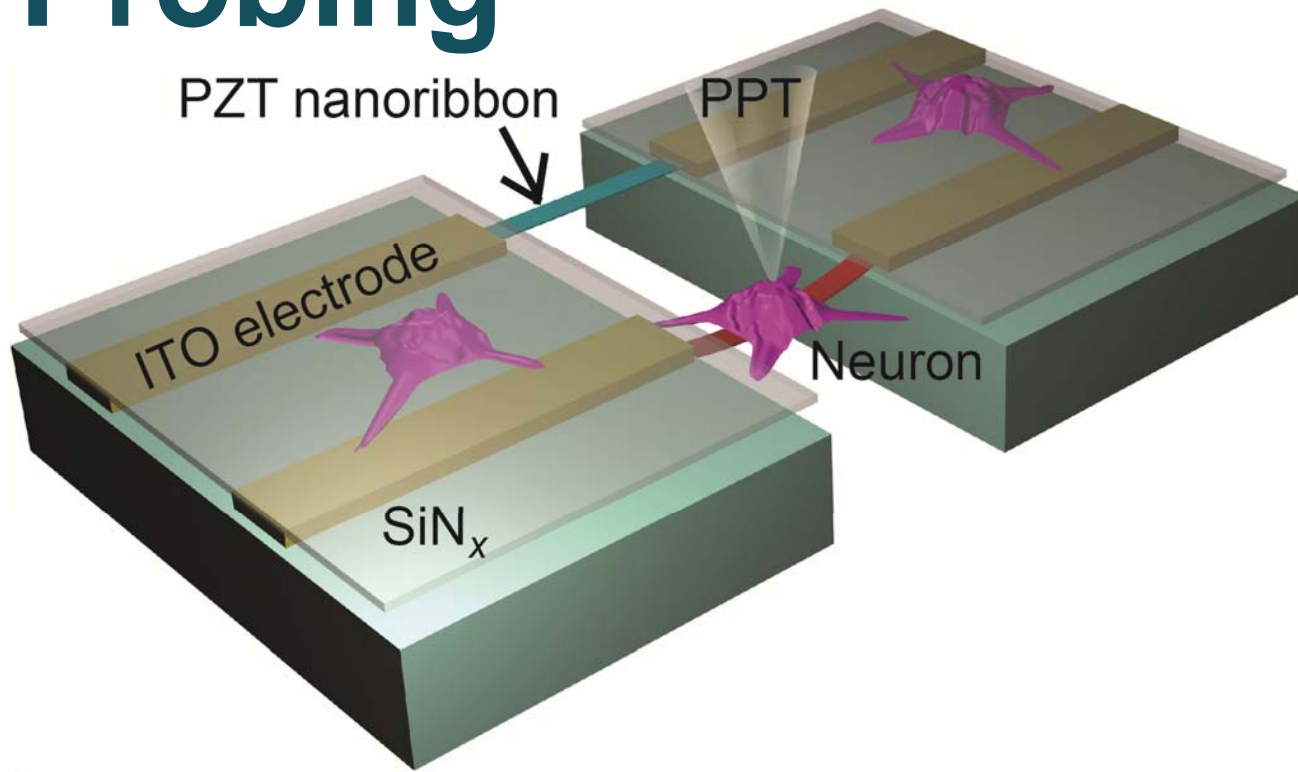
# Cell Nanomechanics



P. Zhang, A. Keleshian & F. Sachs, *Nature* 413, 428 (2001)

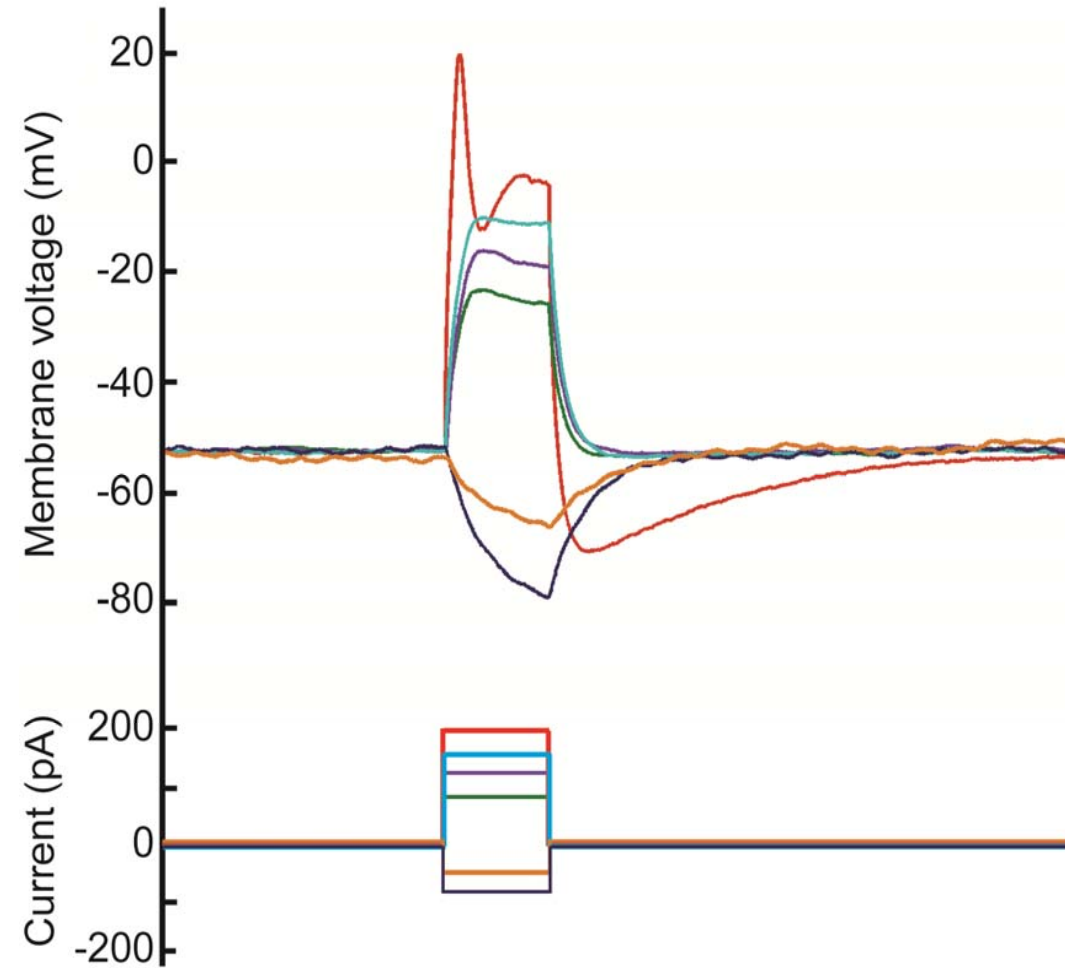
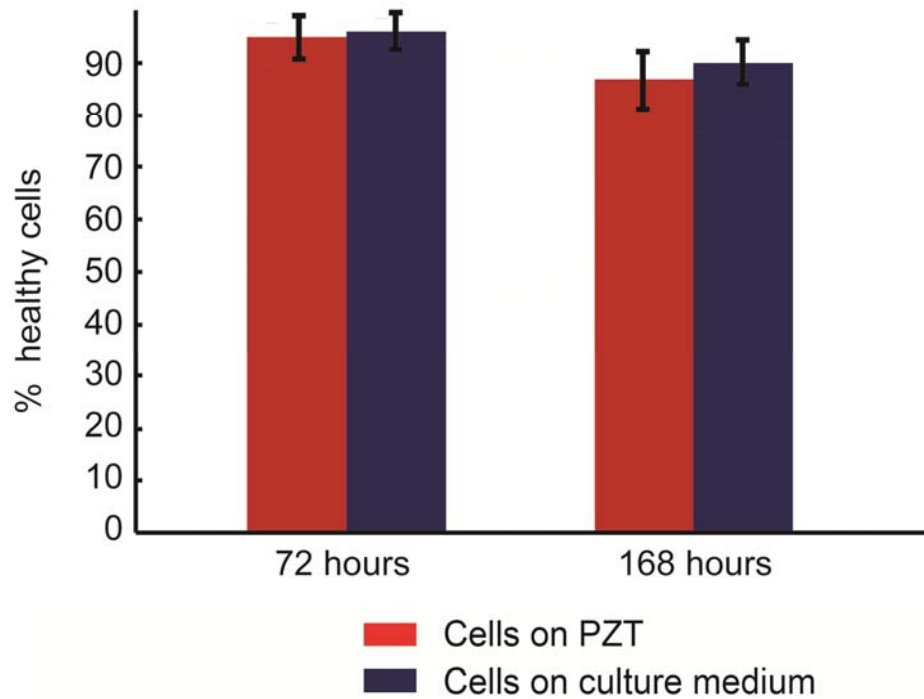
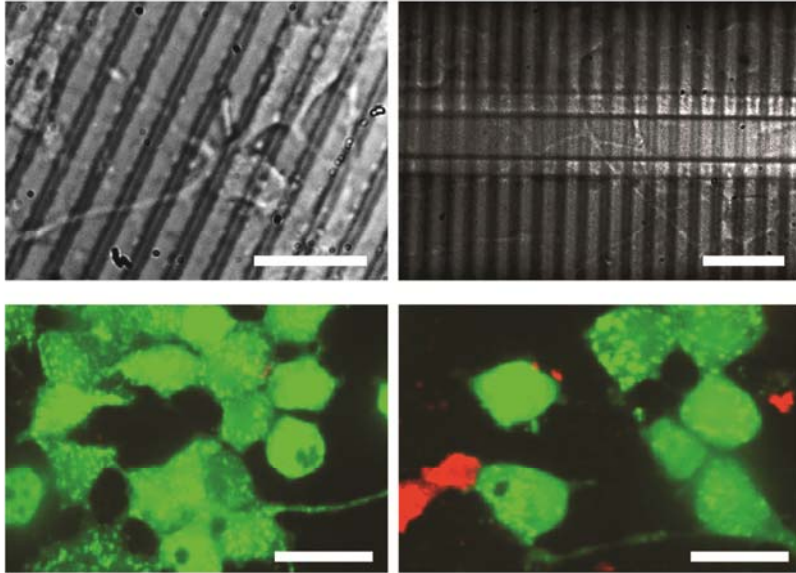


# Piezo-Probing

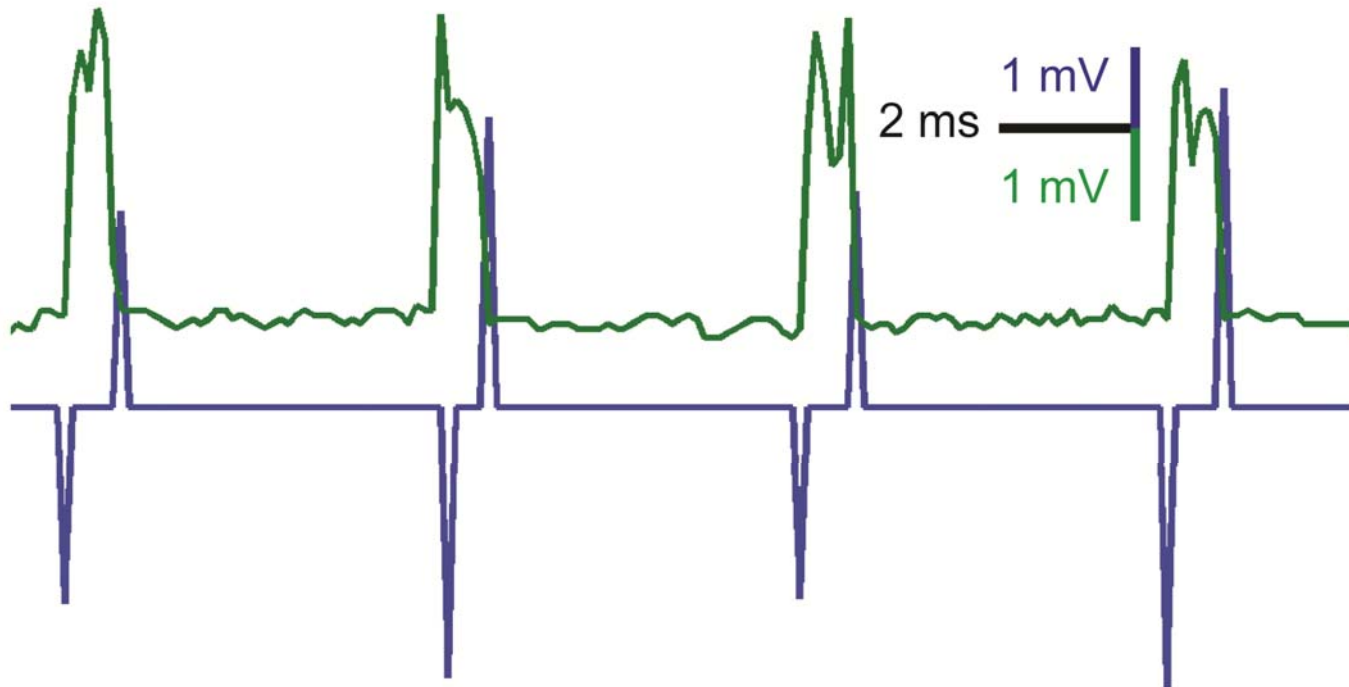
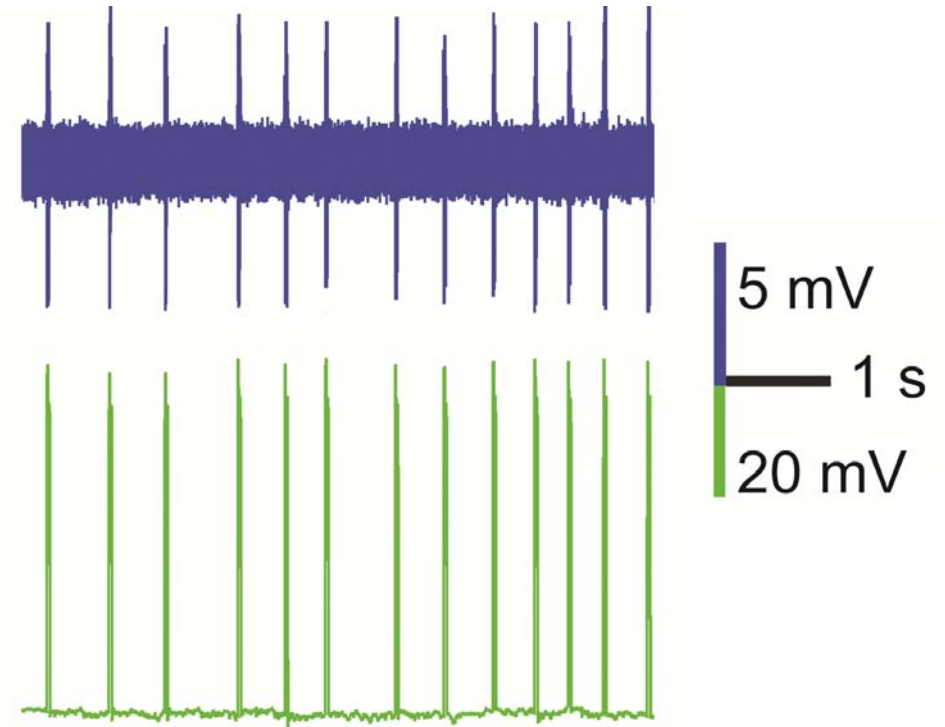
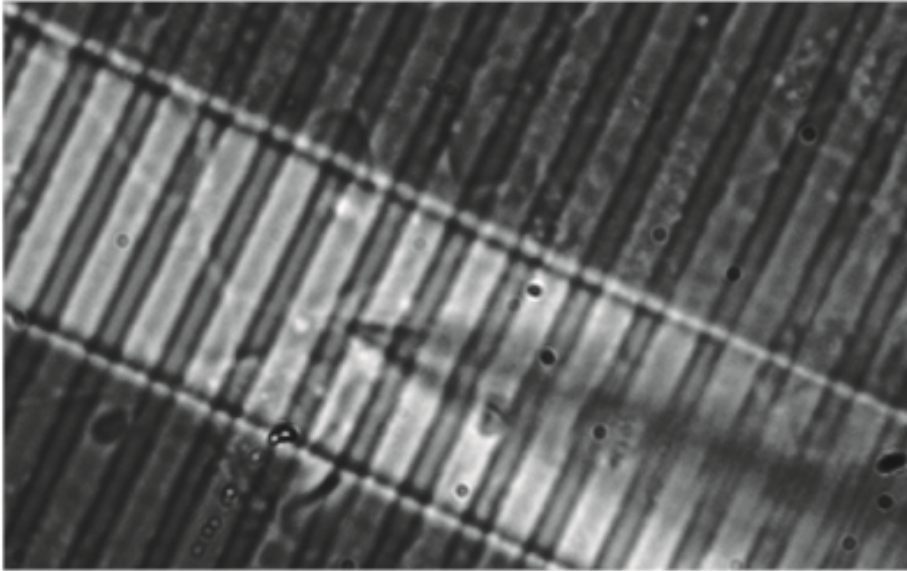




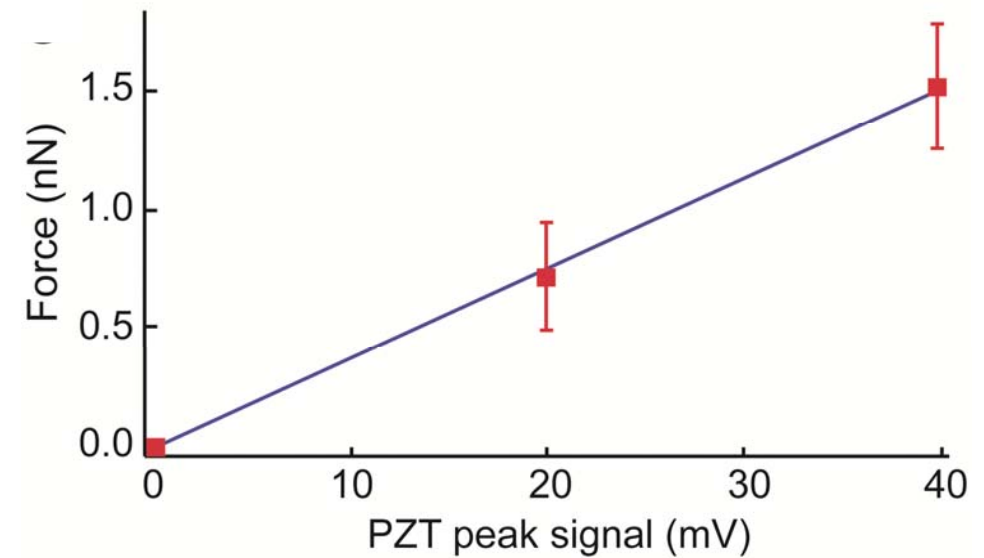
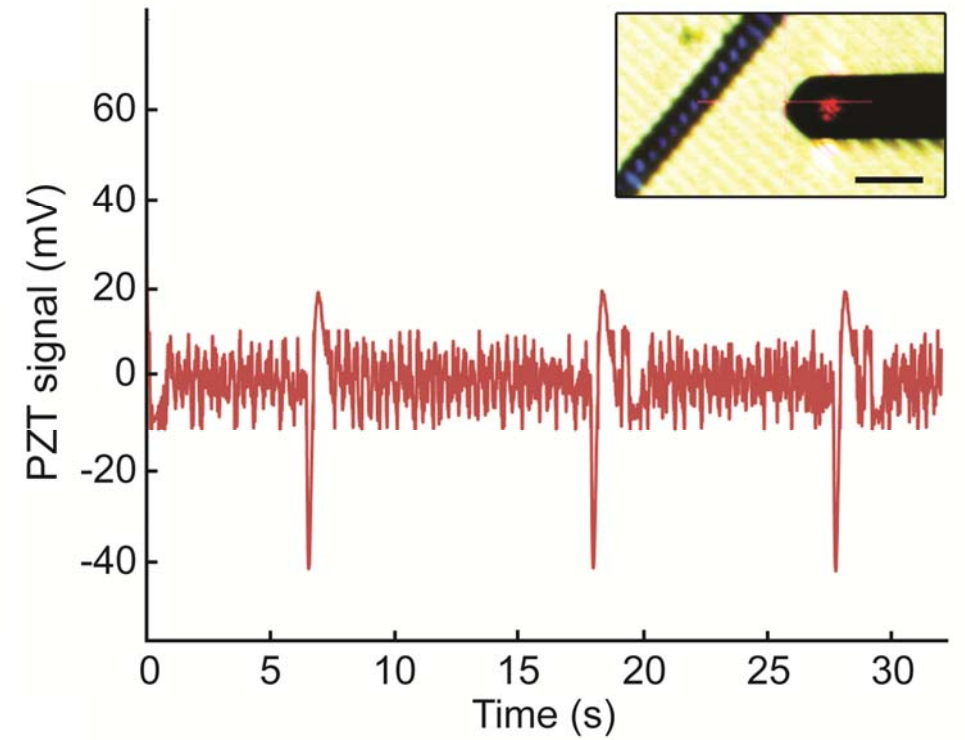
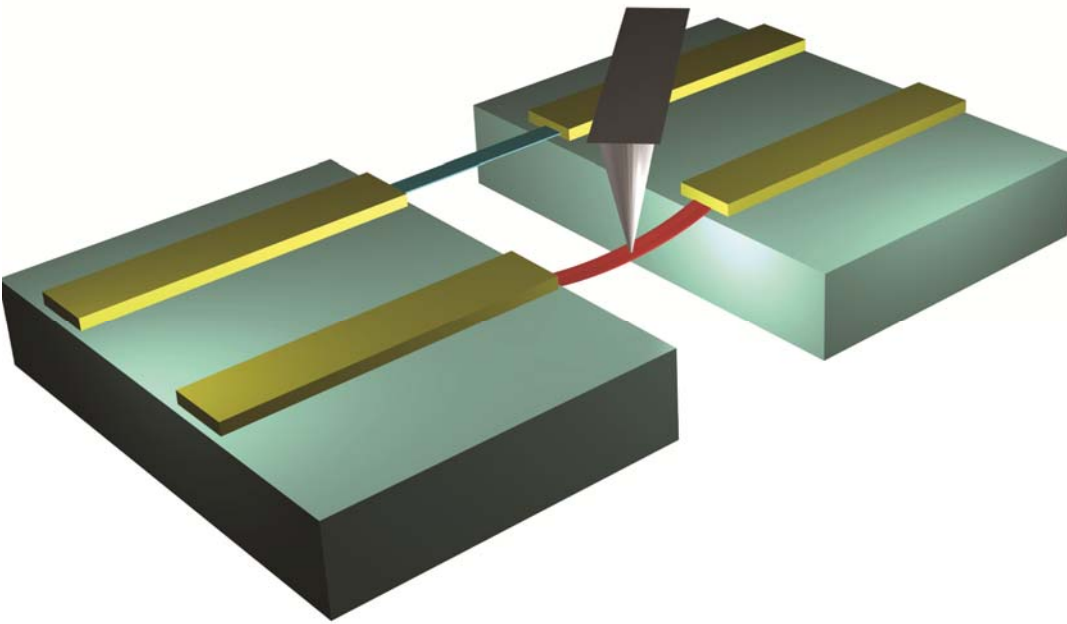
# Viability



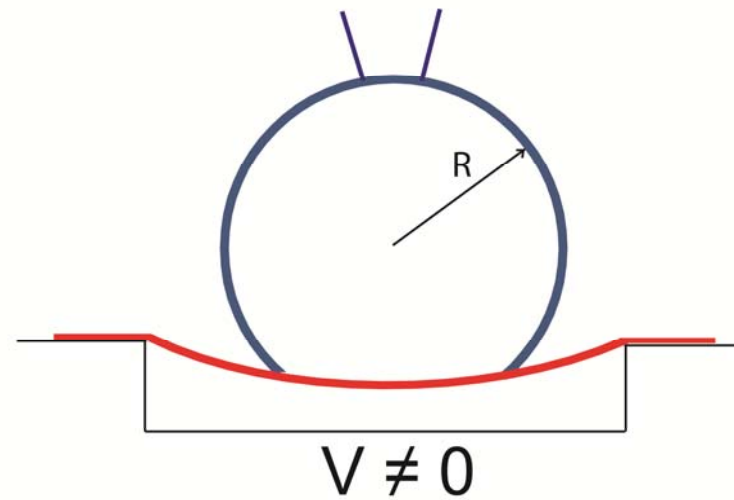
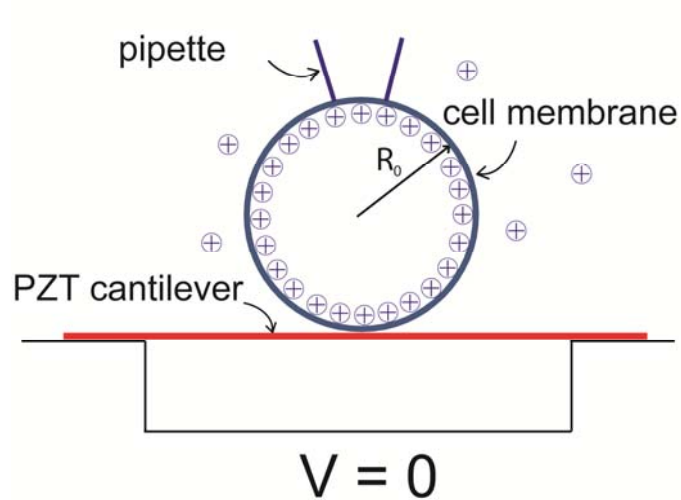
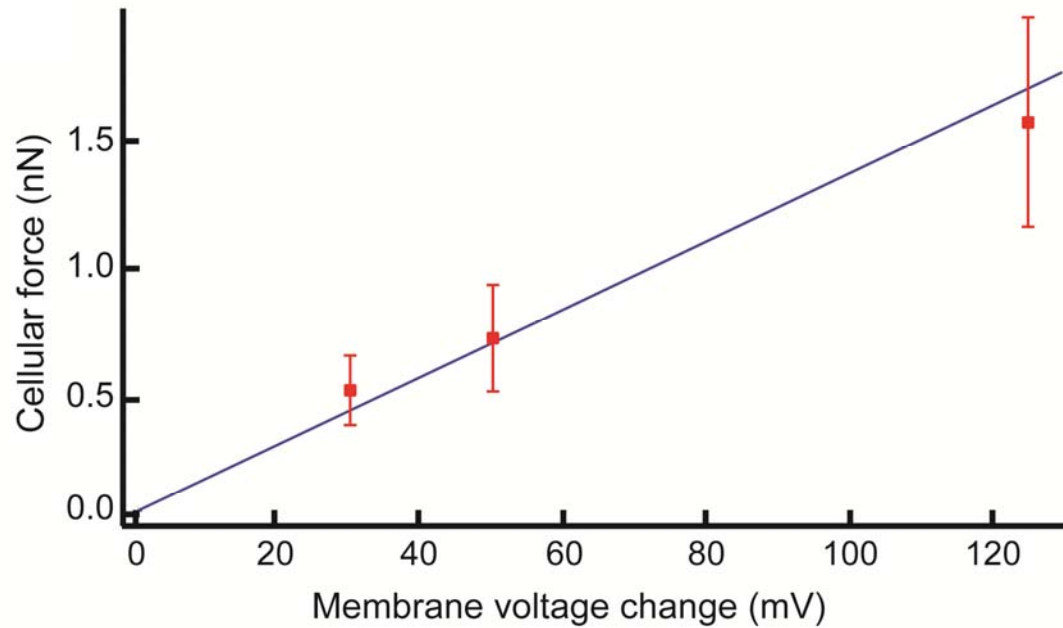
# Neurointerfacing



# Calibration



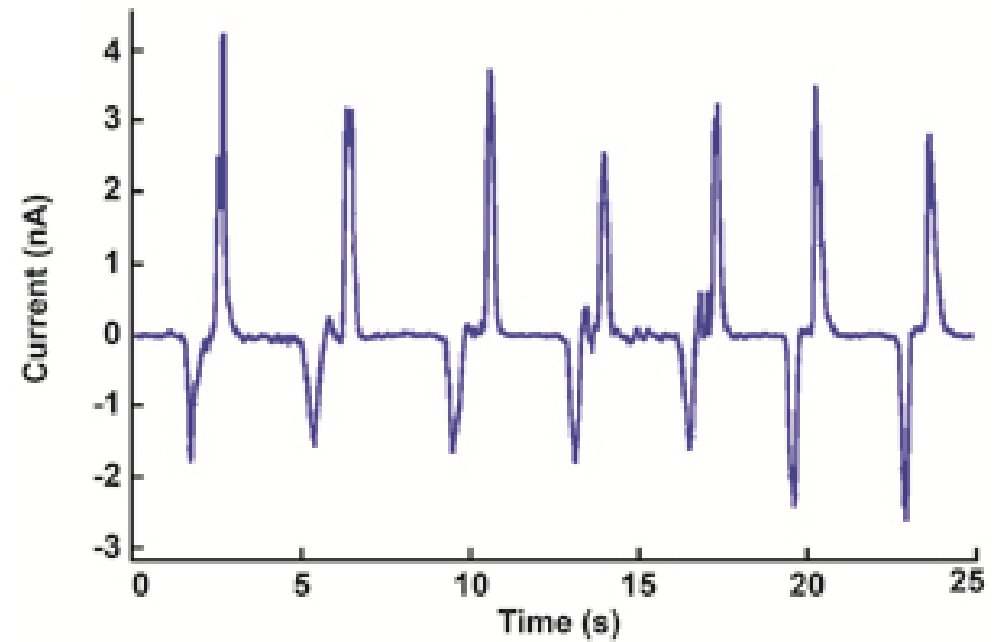
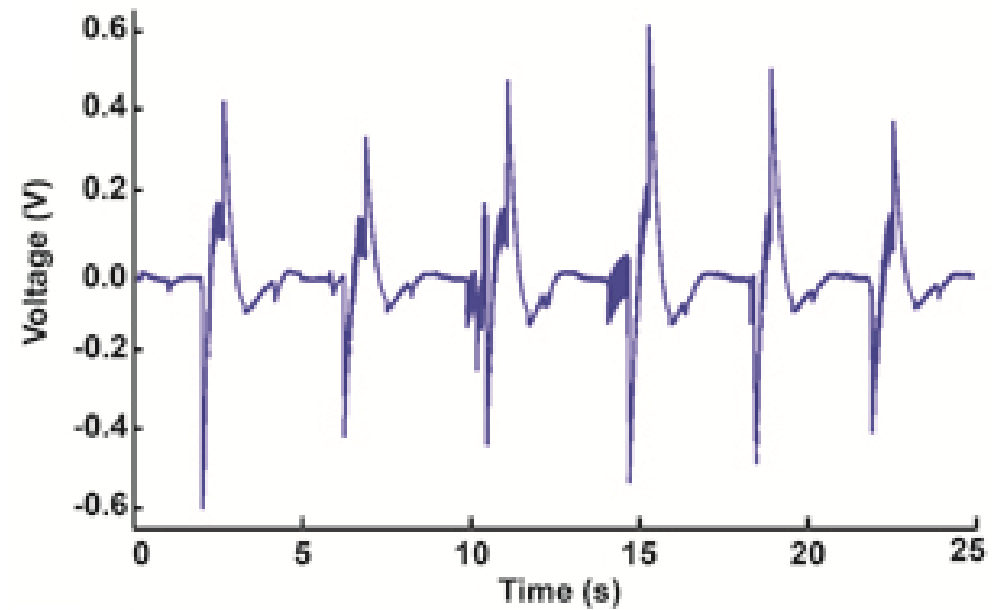
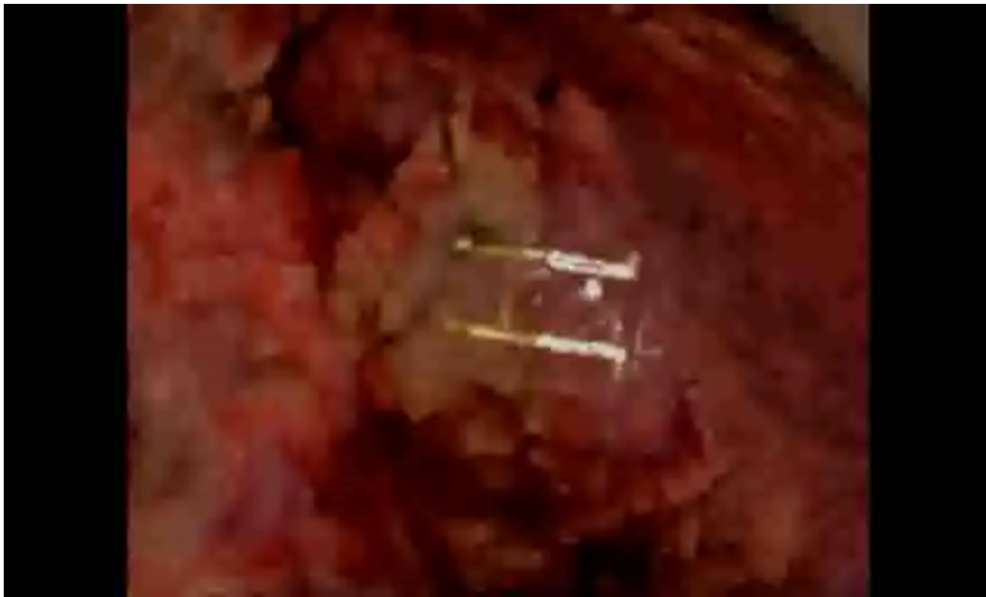
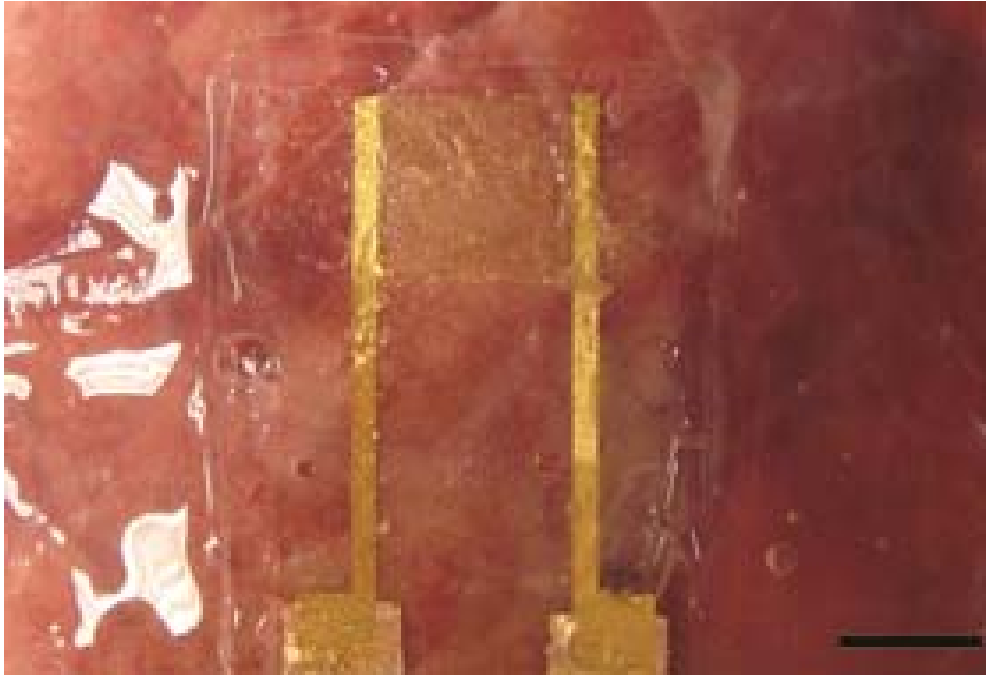
# Quantification



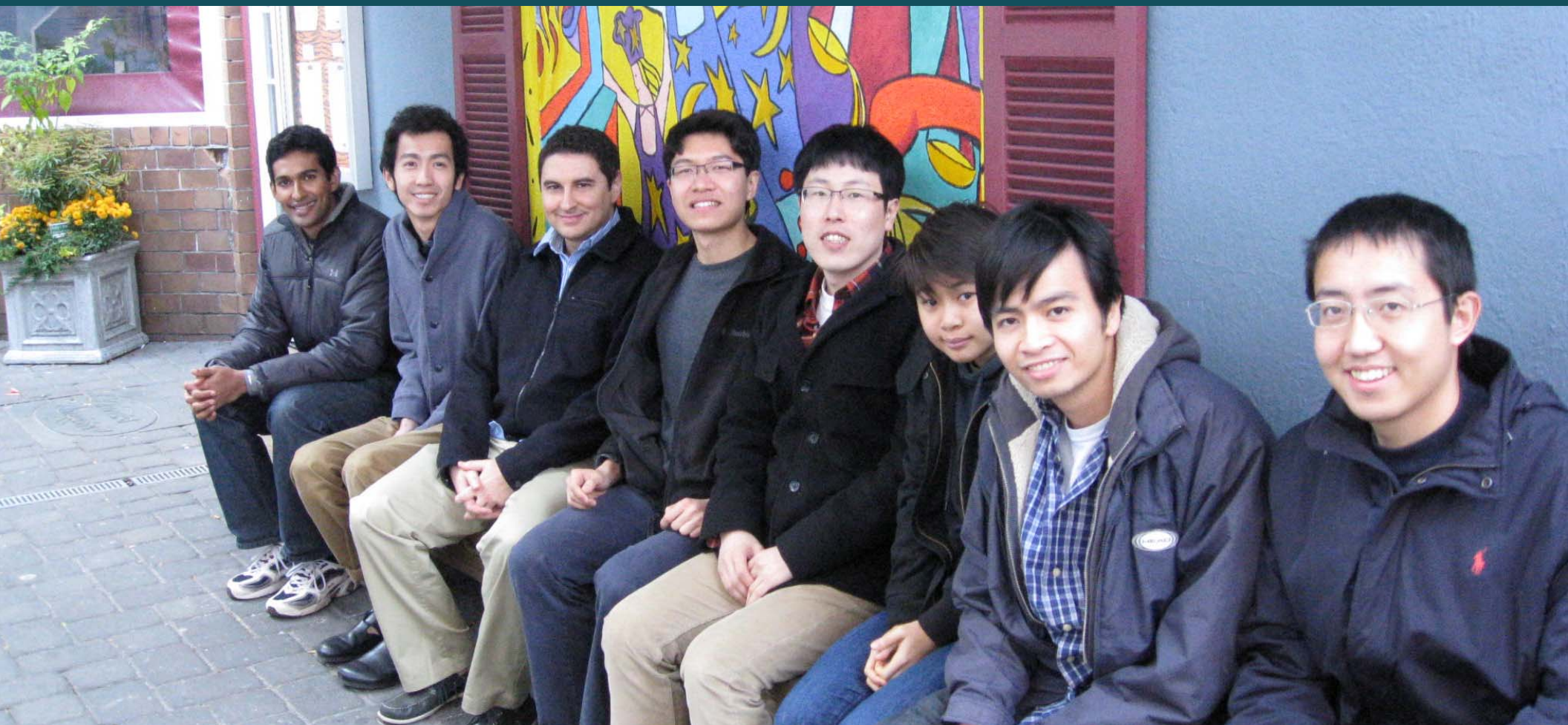
**Force ~ 1.5 nN | Deflection ~ 1 nm**



# Biointerfacing



# Thanks



**DARPA | ARO | LM | AFOSR | AAF | NSF | IC | DUPONT**

**Prashant Purohit (Upenn) | Michael Berry (Princeton)**